Development of a Test Method for Leaching of Lead from Lead-Based Paints Through Encapsulants

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ABSTRACT

Lead in paint has been associated with lead poisoning in children. The use of polymeric encapsulants is a potential abatement method for controlling the exposure to lead from lead-based paints. The objective of this study was to provide a technical basis for a standard test method to measure the transport of lead through polymeric encapsulants. In developing this method, the following variables were investigated: lead pigment type and concentration in the lead-based film, chemical type and pH of leaching solutions, and encapsulant resins. The lead-containing films were prepared using a linseed oil binder. The encapsulants were water-borne epoxy and acrylic products and an oil-based alkyd paint. An experimental setup consisting of a cylinder attached to lead-based film, with and without an encapsulant, applied to a poly(methyl methacrylate) (PMMA) substrate was found suitable for a lead leaching test. A pH controlled system was required and found convenient for controlling the pH of the leaching solutions.

Little (<5 %) lead was leached from a linseed-oil film containing either lead chromate or lead carbonate pigment immersed in inorganic acids or bases in the pH range between 2 and 12, suggesting that little lead would be expected to leach from a lead-based painted wall when the wall comes into contact with weak inorganic acids, or ammonia-based cleaning solutions. Because sufficient lead must be leached from the paint to measure the transport properties of encapsulants, additional leaching agents were investigated. Among the chemical compounds studied, acetic acid was the most efficient lead leaching agent. A pH 2, 3.5 mol/L acetic acid in water leached nearly 70 % lead from a lead carbonate-containing film within 5 hours; this is about 70 times greater than amount of lead leached after 100 hours in a nitric solution of the same pH. Consequently, a leaching solution containing 3.5 moles acetic acid in 1 liter of water was chosen.

For lead-based films under an encapsulant, an induction period exists before lead begins to leach out of the films. After the induction time, a substantial amount of lead leached from the lead-based films under epoxy and acrylic encapsulants and the alkyd paint. The rate in the water-born encapsulants were higher than that of the oil-based alkyd paint. FTIR in the internal reflection mode provided a good method to follow the conversion of acetic acid to lead acetate, and these data were used for determining the diffusion coefficient of lead acetate in a lead-based film. The diffusion coefficient of lead acetate formed from a vinegar solution in a lead-based film was found to be in the same range as other organic acetates, 10^{10} cm^2/s. The diffusion coefficients of 100 % acetic acid in lead-based linseed-oil films, encapsulants, and alkyd paint were measured using a video/computer image analysis procedure; the values are in the 10^{-9} cm^2/s to 10^{-11} cm^2/s range. Acetic acid was found to be a good candidate for leaching lead from a lead-based film with and without an encapsulant covering it.

Keywords: Coating, encapsulant, diffusion, lead, leaching, paint, test method.

Table of Contents

List of Tables

List of Figures

1 INTRODUCTION

Lead in paint has been associated with lead poisoning in children living in tenement buildings (1). According to a recent US Department of Housing and Urban Development (HUD) report, an estimated 57 million homes in the United States contain some lead-based paint[1] (2). Several abatement procedures are being considered for controlling the hazards associated with lead-based paints, including painting over the lead-based paint with a polymeric "encapsulant". Potential benefits of encapsulants include lower cost, less comprehensive requirements for worker protection and containment, and less disruption of the occupant's life as compared to other abatement procedures. Before these benefits can be realized, however, performance requirements, including preventing leaching of lead from the underlying lead-based paint must be established.

Each leaded particle in a lead-based film is covered with a layer of the resin matrix. For lead to leach from a lead-based paint film under an encapsulant, several processes must take place. First, the attacking chemical species must migrate through the encapsulant thickness as well as the resin layer surrounding each leaded particle; second, the leaded particle must be dissolved by the leaching solution; and third, the lead compound(s) formed must be transported outward through the resin matrix and the encapsulants to the solution. Leaching could occur when lead-based films are wetted by rain, condensed water, cleaning solutions, or other liquids.

Methods are available to use in establishing performance criteria to ensure a durable intact paint film (3). However, no test method exists for determining the leaching resistance of polymeric encapsulants. Since measurable leaching of lead to the surface of the encapsulants would be unacceptable, test methods and criteria are urgently needed to investigate leaching resistance of encapsulants. This need has been identified by the ASTM E06.23 Subcommittee on Abatement of Hazards from Lead in Buildings, which has prepared a standard specification on encapsulant coatings.

The objective of this study was to provide a technical basis for the development of a standard method for testing the ability of polymeric encapsulants to control the migration of lead from lead-based paints into the environment. To that end, the effects of variables including lead pigment type and concentration, chemical type and pH of the leaching solutions, and encapsulant resin on the leaching of lead from a lead-based film were investigated. Leaching was studied for lead-based films either covered or not covered by a polymeric encapsulant.

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[1]*Lead-based paint is defined by federal law as paint films having lead contents equal to or exceeding 1 mg/cm^2 or 5 %.*

2 EXPERIMENTAL DESCRIPTION

2.1 Variables

a) Lead Pigment Type: Two types of commercial, leaded pigments were used: lead carbonate and lead chromate. Lead carbonate pigment was obtained from a white paste consisting of a mass fraction of 89 % basic lead carbonate, $2PbCO_3.Pb(OH)_2$, and a mass fraction of 11 % linseed oil. Lead (Pb) accounts for a mass fraction of 80 % of the basic lead carbonate mass. Thus, the lead mass fraction in the lead carbonate pigment was 0.71 (0.89 x 0.8). The lead chromate pigment, which contained approximately a mass fraction of 60.0 % lead, was a 100% mass fraction lead chromate, $PbCrO_4$. The solubilities of lead carbonate and lead chromate in water at 22 °C are so low (approximately 2 mg/L H_2O and 0.2 mg/L H_2O, respectively (4,5)) that both pigments are considered to be insoluble in water at ambient temperature. Basic lead carbonate is slightly soluble in alkali and dilute nitric acid solutions and soluble in acetic acid, while lead chromate is slightly soluble in alkali and dilute nitric acid solutions but insoluble in acetic acid.

b) Lead Concentration: Two lead concentrations in the films: mass fraction of 54 % (low) and mass fraction of 71 % (high) were investigated.

c) pH of Leaching Solutions: 2, 4, 10, and 12. These pH values cover the range of most household materials, such as vinegar (pH=2.5) and ammonium-based cleaning agents (pH=12).

d) Leaching Solution Chemicals: Common acids and bases and household chemicals were investigated. These include: nitric acid (HNO_3), acetic acid (CH_3COOH), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), and vinegar (vinegar contains approximately a mass fraction of 5 % of acetic acid).

e) Encapsulant and Paint Type: Two water-borne, commercial encapsulants based on epoxy and acrylic resins, and one alkyd paint were selected. These resins are among the most common materials used in paints and encapsulants. All three products contained titanium dioxide pigments. The amounts of pigment, resin, and other components in the encapsulants and alkyd paint were unknown. It should be emphasized that these materials may not be typical of all encapsulants used for controlling lead in lead-based paints.

2.2 Specimen Preparation

2.2.1 Specimens for Leaching Test

White lead paste, containing a mass fraction of 89 % basic lead carbonate and a mass fraction of 11 % linseed oil, was used to provide the 71% mass fraction lead concentration (high) films. For the films containing 54 % mass fraction lead (low), the formulation consisted of a mass fraction of 76% basic lead carbonate and a mass fraction of 24 % boiled linseed oil. The 54 % mass

fraction lead formulation is typical of a lead-based paint used prior to the introduction of TiO_2 pigment. All leaching studies were performed on specimens of lead-based films on a transparent poly(methyl methacrylate) (PMMA) substrate (Figure 1). It is noted that lead-based paints are commonly found on wood in old buildings, but wood is a very difficult material to characterize for a test procedure. Further, cellulose, hemicellulose, and solvent-extractable materials in wood are liable to be attacked by acids and bases. This would be undesirable in this study because the leaching solutions can be highly acidic or basic. On the other hand, PMMA is a chemically-inert, well-specified, polymeric material, and therefore, a good choice as a model substrate.

Lead-based specimens were prepared by applying a thoroughly-mixed lead paste on 60 cm x 20 cm x 0.6 cm PMMA substrate using a blade applicator having a 125 μm gap. The films were cured by exposing them for three days at ambient conditions (23 °C and approximately 45 % relative humidity) followed by three days in an air-circulated oven at 60 °C. Under these conditions, the lead-based films appeared to completely cure, as determined by differential scanning calorimetry (DSC). The dry film thickness of the high-lead film was 93 μm and of the low-lead film was 54 μm; their respective densities were 3.7 g/cm^3 and 2.4 g/cm^3.

After curing, half of the coated samples were covered with an encapsulant. For unencapsulated specimens, the lead-based film coated PMMA substrates were cut (by saw) to a 10 cm x 10 cm size. For tests with an encapsulant, the encapsulant was applied to the lead-based film coated substrate using a 650 μm gap blade applicator. The encapsulants were allowed to cure following the manufacturers' recommendations. The thicknesses of the cured epoxy and acrylic encapsulants, and alkyd paint on the lead-based film were 230 μm$\pm$8 μm, 350 μm $\pm$14 μm and 220 μm $\pm$12 μm, respectively. Hereafter, specimens of lead-based films on the PMMA substrate with and without an encapsulant are designated as encapsulated and unencapsulated lead-based specimens, respectively.

Two types of lead-based specimens were prepared, as shown in Figure 1a (Type I) and Figure 1b (Type II). It is noted that the Type I specimen was completely immersed in the leaching solution, while only the surface of the Type II specimen was exposed to the leaching solution. Type I specimens consisted of a lead-based film on a PMMA substrate. These specimens had a dimension of 10 cm x 10 cm x 0.6 cm, which were cut from the 60 cm x 20 cm x 0.6 cm samples. The edges of each specimen were sealed with paraffin wax (Figure 1a) to ensure that the leaching solution only entered the film through the top surface of the specimen and to prevent the delamination of the film from the substrate during immersion. Delamination complicated the analysis of lead leaching because both faces of the film were then exposed to the leaching solution.

Type II specimens were prepared by attaching a poly(vinyl chloride) (PVC) cylinder having an inside diameter of 10.8 cm and a height of 9.5 cm to the surface of a 15 cm x 20 cm dimension, film-coated PMMA substrate, using a room-temperature silicone adhesive. Wax was used to seal the outside bottom of the cylinder to prevent leaking. The PVC cylinder was used to contain the leaching solutions. The area (90.0 cm^2) within the cylinder was the area of the lead-based film specimen in contact with the leaching solution. The lead-based film volume within the cylinder
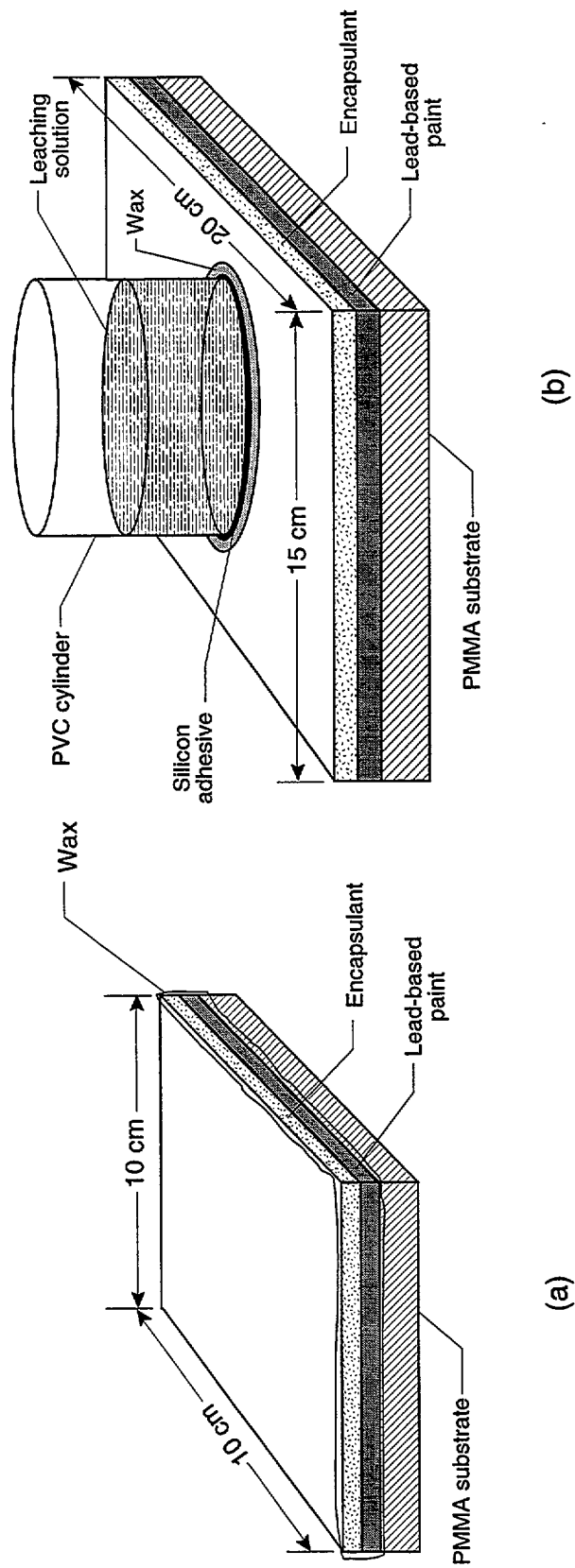
3

Figure 1. Types of specimen used for lead leaching experiment from a lead-based film with and without an encapsulant applied to it; a) Type I and b) Type II.

was 0.49 cm³ (90.0 cm² area x 0.0054 cm film thickness). It will be shown that the Type II specimen configuration was preferred for most of the lead leaching tests because it eliminated the problem of a lead-based film delaminating from the substrate.

It was important to determine the total amount of lead in each specimen because the amounts of lead leaching from the film were ratioed against the original amounts of lead in the film. This ratio, which determined how much lead leached out of a lead-based film, allowed a comparison of the effects of the different experimental variables. The amounts of lead in the high-lead (mass fraction 71 %) and low (mass fraction 54 %) films of Type I specimens were found to be 2.47 g and 0.70 g, respectively. The calculation for the high-lead film was based on the following data: 10 cm x 10 cm side dimension, 93 μm thickness, 3.8 g/cm³ density, and 0.71 lead fraction in the film. The amount of lead in the low-lead film was computed using the same side dimension, 54 μm film thickness, 2.4g/cm³ density, and 0.54 lead mass fraction. Using the same procedure, the amount of lead in the 54 % mass fraction lead film within the cylinder of Type II specimen was 0.64 g (0.49 cm³ volume x 2.4 g/cm³ density x 0. 54 lead mass fraction). It should be noted that all Type II specimens were low-lead films.

2.2.2. Specimens for Lead Diffusion Measurement

In addition to the specimens of film applied to a substrate, which were used in the leaching experiment, free films of lead-based and alkyd paints and encapsulants were also prepared for measuring the diffusion coefficients of leaching agents in these materials. Free films were prepared by applying lead-based and encapsulant formulations on release paper. The coated films were cured using the same schedules for curing the films applied to the PMMA substrate. After curing, they were removed from the release paper and conditioned at ambient environments for two weeks. The thickness of the lead-based free film was 54 μm $\pm$ 7μm and those of the alkyd paint, epoxy encapsulant, and acrylic encapsulant were 70 μm $\pm$ 2 μm, 80 μm $\pm$ 7 μm, and 74 μm $\pm$ 5 μm, respectively.

2.3 Lead-Leaching Experiment

2.3.1 Instrumentation

The solubility of lead in a solution depends strongly on the pH and chemical nature of the solution. Further, the pH of the leaching solution may affect the rate of lead leaching from a lead-based organic film. In a preliminary experiment, we observed that the pH of various organic coatings and encapsulants immersed in distilled water varied widely and that the pH of these materials in distilled water changed with immersion time, as shown in Table 1. We made an effort to control the pH of the leaching solutions within a narrow range during the leaching experiment. Initially, we controlled the pH of leaching solutions with buffer solutions. However, our preliminary tests indicated that the presence of a buffer strongly influenced the concentration of lead materials in the leaching solution. For this reason, another approach was developed where

the pH was controlled automatically by adding an amount of acid or base to the solution until the pH fell within the desired range again. This approach was found reliable and used throughout the study.

Table 1. Changes in pH of paints and encapsulants with immersion time in distilled water

	pH	
Sample	**24-hour immersion**	**48-hour immersion**
Alkyd paint 1	3.5	4.2
Alkyd paint 1 + lead chromate pigment	4.2	4.1
Alkyd paint 2	6.4	6.4
Alkyd paint 2 + lead carbonate pigment	4.6	4.0
Acrylic encapsulant	9.7	10.0
Epoxy encapsulant	6.6	6.9
Distilled Water	7.6	7.6

Figure 2 schematically presents the experimental setup used for maintaining the solution pH, while Figure 3 shows a photograph of two apparatuses. The components of the automatic pH controlled system (Cole Palmer Model 05652)[2] are a pH/mV/temperature controller, a magnetic stirrer, a solution container, and two burettes with electrically adjustable valves. The valves are coupled to a pH sensor, which is connected to the pH controller. One burette contained an acid solution while the other contained a base. The acid and base in the burettes were used for adjusting the pH of the leaching solution. The type of the acid and base pair depended on the type and pH of the leaching solutions. For example, HNO_3 and $NaOH$ at suitable concentrations were used for nitric and sodium hydroxide leaching solutions, HNO_3 and NH_4OH for ammonia, and CH_3OOH and $NaOH$ for acetic acid and vinegar. Further, the concentration of the acid and base depended on the pH of the leaching solutions. The more alkaline or acidic a leaching solution was, the more concentrated was the respective base or acid, used. The accuracy of the pH control was within 0.1% for the pH range from 0 to 14.

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[2] *Trade names are given solely to indicate experimental materials and equipment used and are not meant to recommend a particular product by the National Institute of Standards and Technology or to imply that it is the best available for the experiment.*

100 ml burette

Support

100 ml burette

Acidic solution

Basic solution

Electric actuated valve

Electric actuated valve

Digital readout

pH electrode

Sample

pH = 7.6

Stir bar
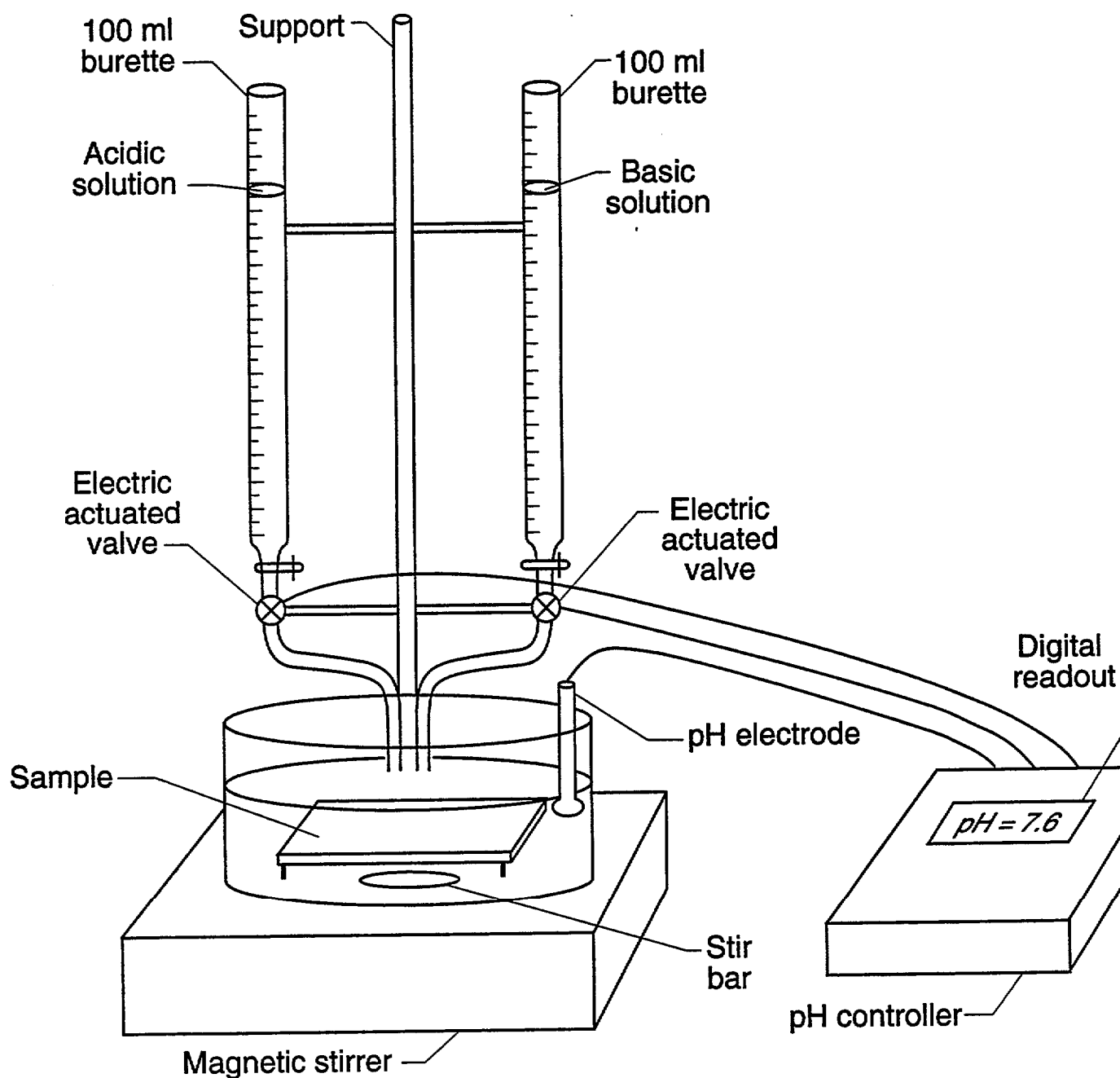
Magnetic stirrer

pH controller

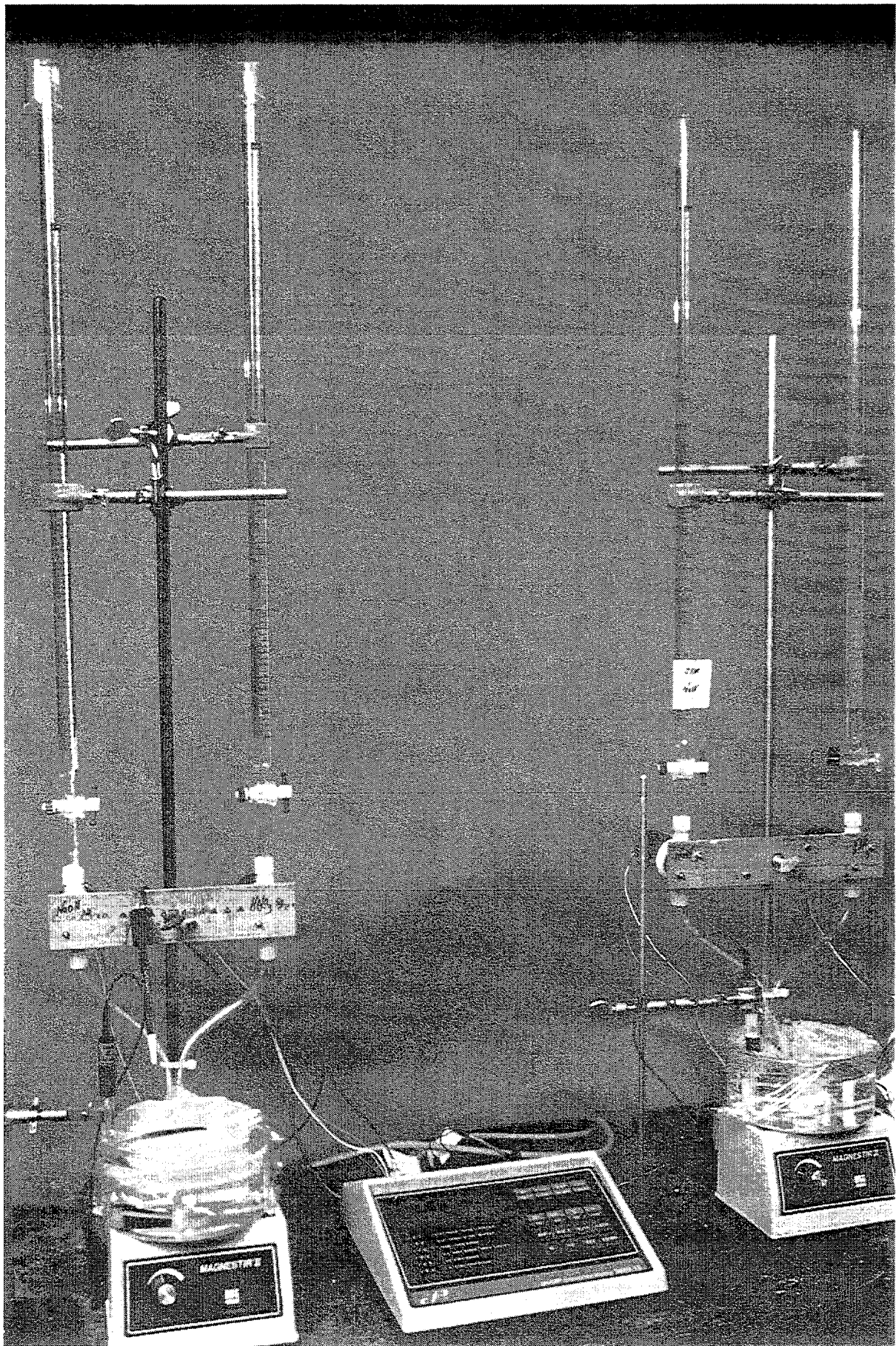*Figure 2. Experimental setup for controlling pH of leaching solution.*

Figure 3. Photograph of two test apparatuses.

2.3.2 Leaching Procedure and Analysis

To start a leaching experiment, a known volume of the leaching solution of between 500 mL and 750 mL was poured into the container (glass container for Type I and PVC cylinder for Type II specimen). Acid and base solutions having appropriate pH values were placed into the respective burettes. Once the pH controller was turned on, drops of acid or base from the burettes were automatically added to the leaching solution until the preset pH was reached. The solution was continuously stirred using a magnetic bar. At specified intervals, a volume of 5 mL to 10 mL of the leaching solution was removed from the container, filtered, transferred to a glass test vial, and analyzed for lead content. Unless otherwise stated, flame atomic absorption (FAA) spectroscopy was used for measuring lead content in the leaching solutions. The pH of all test solutions was controlled to within $\pm$ 0.1 of the desired value. All leaching experiments were conducted at ambient conditions (22 °C and approximately 45 % relative humidity). Lead reference solutions were used to calibrate the FAA instrument. To ensure the accuracy of the FAA instrument in all concentration ranges, lead reference solutions at different concentrations were used to establish an intensity/concentration curve. This was done for each pH. All measurements of lead in the leaching solution were expressed as mass concentration, i.e., grams of lead in one liter of the solution.

2.4 Other Characterization Techniques

Besides the FAA technique, a number of other analytical methods were employed to characterize the films before and after immersion in the leaching solutions, including scanning electron microscopy (SEM), spot x-ray analysis, light microscopy, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and video-computer image analysis. Specimen preparation and procedures used in making these measurements are briefly described below.

a) **Scanning Electron Microscopy and Spot X-Ray Analysis.** These techniques were used to identify lead pigments and their distribution in the lead-based paint films. Specimens were prepared by imbedding a 12 mm x 12 mm lead-based film in an epoxy potting compound, which was enclosed in a mold. After the potting compound hardened, the imbedded block was removed from the mold, cut (cross section of lead-based film), polished, and coated with a layer of gold (to prevent charging). The SEM micrographs were taken in the backscattered mode using a 10 keV voltage at magnifications of 700 x and 4000 x. Spot x-ray analysis of the leaded particles was performed after magnifying the SEM image to 100,000 x.

b) **Light Microscopy.** This instrument was used to examine the surface appearance of the encapsulants. A camera was attached to a light microscope, and pictures of specimen surfaces were taken.

9

c) Differential Scanning Calorimetry (DSC). The DSC technique was employed to determine the degree of cure in the lead-based films and encapsulants. Dry free films of lead-based paints and encapsulants having a mass between 20 mg and 25 mg were placed in an open aluminum pan. For lead-based paint, a sample of the uncured material was also analyzed. The analysis was carried out in the 0 °C to 200 °C temperature range at a heating rate of 20° C/minute using a modulated differential scanning calorimeter. Nitrogen was used as the purge gas.

d) Fourier Transform Infrared Spectroscopy. When a lead-based film is immersed in vinegar, lead acetate is formed. The formation of lead acetate was followed using FTIR in the multiple internal reflection mode (FTIR-MIR). The measurement utilized a horizontal attenuated total reflection (HATR) accessory with a ZnSe prism. A screen-supported 1.2 cm x 5 cm specimen of a lead-based free film was placed parallel to the bottom surface of the HATR trough. A volume of the leaching solution was added to the trough so that the specimen was completely immersed. After placing the HATR accessory with the specimen in the spectrometer, FTIR-MIR spectra of the solution were taken *in situ* as a function of time. All spectra were recorded at a 4 cm^{-1} resolution and were a co-addition of 32 scans. Difference spectra were obtained by subtracting the spectra of unexposed specimens from the spectra of specimens immersed in solutions at different times. This was done after scaling so that all spectra have the same intensity of the CH band at 2926 cm^{-1}. In this way, errors due to sampling were minimized. Peak height (distance between the peak and the base line) was used to express FTIR intensity.

e) Video-Computer Image Analysis. This technique was used to measure the swelling and the diffusion coefficients of 100 % acetic acid in encapsulants and lead-based films. Free films of approximately 2.5 cm x 2.5 cm were immersed in petri dishes containing 100 % acetic acid. Changes in the X and Y directions of the films as a function of exposure time were captured using a video camera. Image analysis was used to calculate dimension and volume changes, assuming that swelling in all films was isotropic. The swelling was expressed as percent change of specimen initial volume. The results are the average of four specimens.

3 RESULTS AND DISCUSSION

3.1 Degree of Cure of Lead-Based Films

Each lead pigment particle in a lead-based paint is imbedded in the resin matrix of the paint. In order for lead to leach from the lead-based film, the lead must be transported by the leaching agent through the resin matrix. This transport process is similar to that of any chemical species in a polymer coating. That is, it depends on the microstructure of, and the diffusivity of the lead species in the coatings. These properties are a function of the state of cure of the films. A properly-cured paint film is a good barrier to the transport of most cations while an under-cured film provides regions with easy access to the cations.
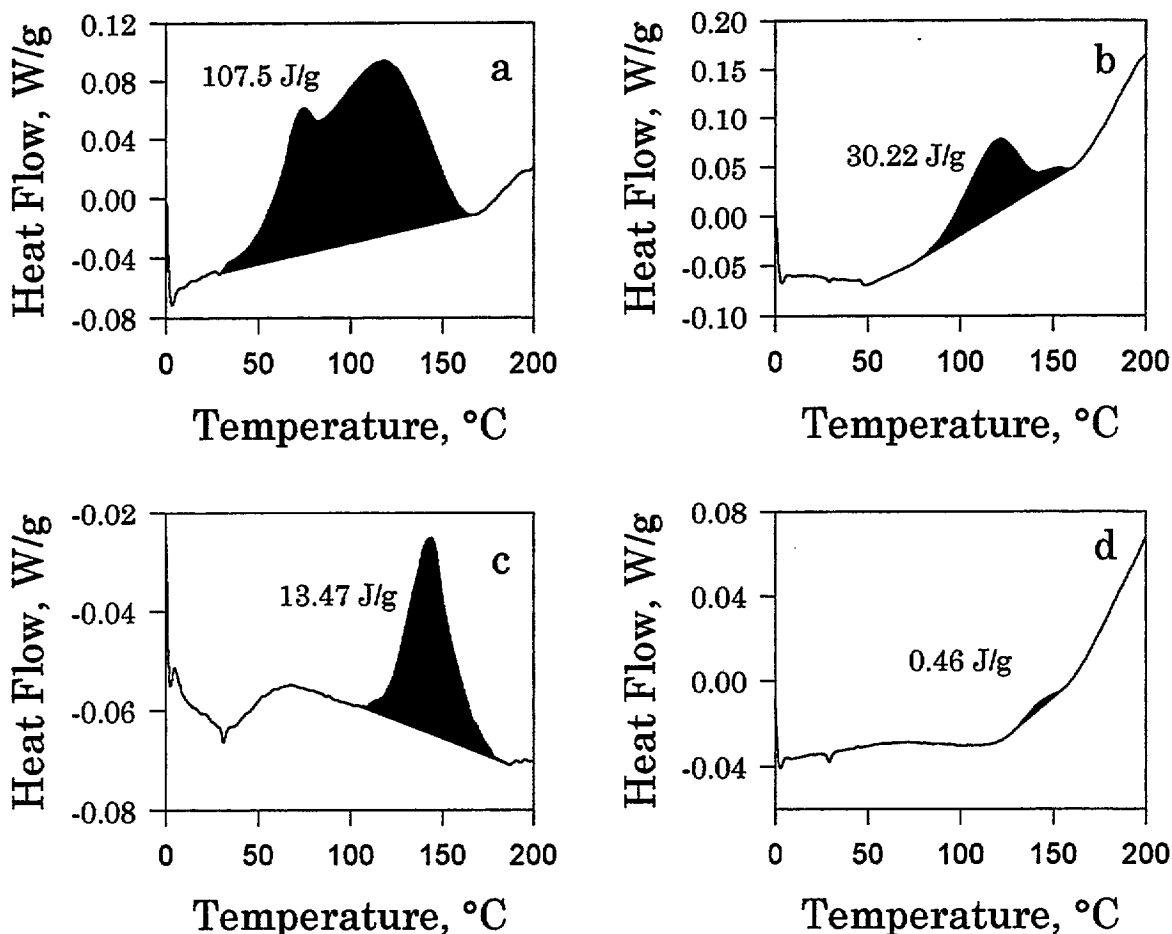
Figure 4. Differential scanning calorimetric curves of lead-based film cured at: a) before curing; b) 5 weeks at ambient; c) 5 d (day) at ambient + 2 d at 60 °C; and d) 3 d at ambient + 3 d at 60 °C.

In this study, the state of cure of the lead-based films and encapsulants was measured using the peak areas on the DSC curves. The peak area of a DSC curve is proportional to the amount of heat (enthalpy) produced by a physical or chemical change in the films. For linseed oil, the curing is an oxidative process that liberates heat. Thus, the DSC curves of an uncured or partially-cured linseed-oil film using air as the environment in the heating chamber should exhibit exothermic peak(s) corresponding with the oxidative reactions. These exothermic areas are proportional to the amounts of the unreacted chemical groups in the film.

Figures 4a to 4d are the DSC curves for a lead-based, linseed-oil film that has been cured under different conditions. Included in these curves are the enthalpy values generated by the oxidative curing reactions of a linseed-oil material. The curve of the uncured paint (Figure 4a) has a broad exotherm extending from 28 °C to 167 °C and peaking at about 75 °C and 117 °C. This sample produced an exothermic enthalpy (indicated in the shaded area) of approximately 107 Joule per

gram (J/g) of the paint. The results of Figure 4b indicate that curing at ambient conditions was not effective for this type of paint, as evidenced by a high enthalpy value produced by unreacted chemical groups in the film. Even after five days of curing at ambient conditions plus two days post-cure in an air-circulated oven at 60 °C, the films were not completely cured, as evidenced by the presence of a substantial enthalpy value (13 J/g in Figure 4c). However, after a post-cure for three days in the oven at 60 °C, the films were completely cured, as shown in Figure 4d. Obviously, temperature was an important factor in curing the lead-based linseed-oil films. Based on these results, a curing schedule consisting of three days at ambient conditions followed by three days in an air-circulated oven at 60 °C was chosen.
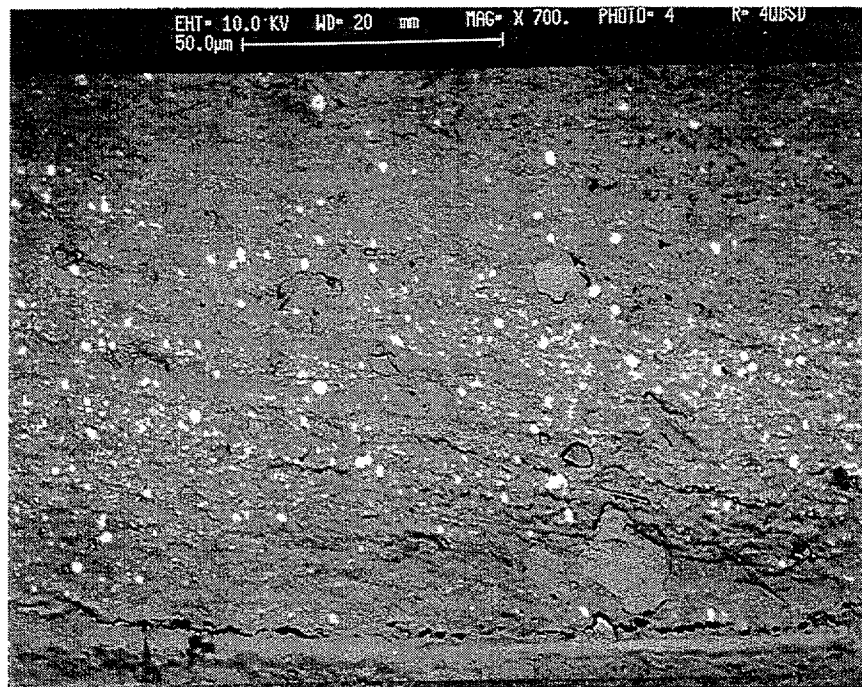
As indicated earlier, the curing of the encapsulants and the alkyd paint was based on the manufacturers' recommendations. Epoxy and acrylic encapsulants and alkyd paint appeared to have cured completely before conducting the leaching experiments, as evidenced by the DSC curves of these materials.

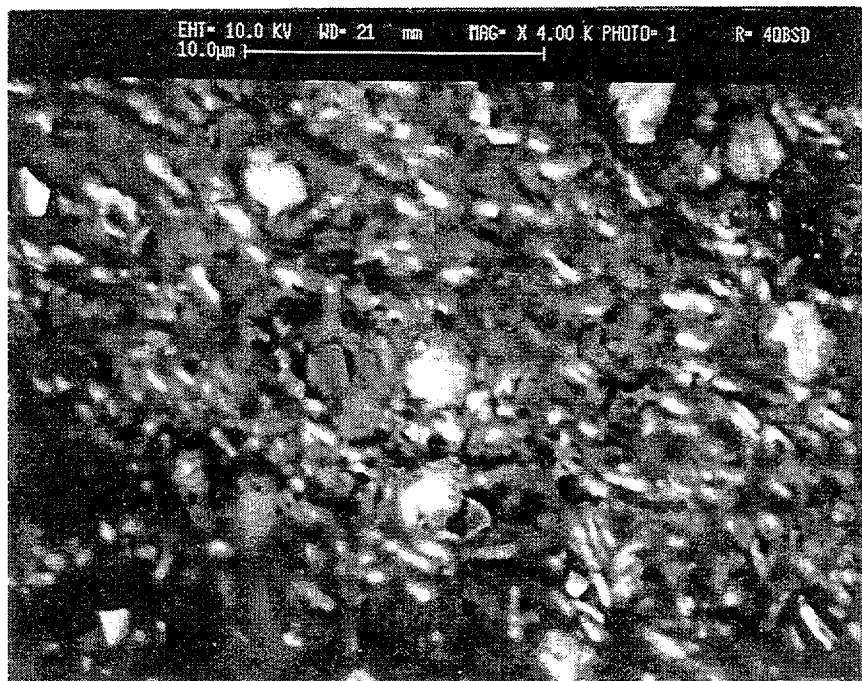## 3.2 Quality of Lead-Based Films and Encapsulants

In addition to the state of cure, the integrity and microstructure of the film may affect the transport of lead derivatives through a film. The cross sectional microstructure of lead-based films was studied by scanning electron microscopy (SEM) in the backscattered mode (to enhance the contrast between resin and leaded particle). The surface appearance of the encapsulants on lead-based films was examined by light microscopy, as stated in the Experimental Section. Figures 5 and 6 are the SEM micrographs of cross sections of the 54 % mass fraction and 71 % mass fraction lead-based films, respectively. Figures 5a and 6a were taken at a 700x magnification and Figures 5b and 6b were at 4000x magnification. In Figures 5 and 6, the outside face of the film is at the top and the underside is at the bottom of the micrographs. The bright spots in these pictures correspond to leaded particles.

Figures 5 and 6 show that substantially more leaded particles lay at the bottom of the 71 % mass fraction lead film than at the top, while both faces of the 54 % mass fraction lead film appeared to be deficient of leaded particles. As seen in Figures 5b and 6b, there are two types of leaded particles in the basic lead carbonate used in this study: circular and plate. Spot x-ray analysis indicated that the circular particles contained higher lead (Pb) and carbon © contents than the plate-like particle. Close examination of these photographs, at low and high magnifications, revealed many cracks in the cross sections of the films. These cracks probably resulted from the severe conditions used during the SEM analysis, because the surface of these films appeared smooth before they were placed in the potting molds.

The surface appearance of the epoxy and acrylic encapsulants are displayed in Figures 7a and 7b. The surface of the epoxy encapsulant films contained a large number of bubbles and pinholes (Figure 7a) while the acrylic encapsulant had a wavy appearance (Figure 7b).

EHT= 10.0 KV   WD= 20 mm   MAG= X 700.   PHOTO= 4   R= 40BSD
50.0μm

a

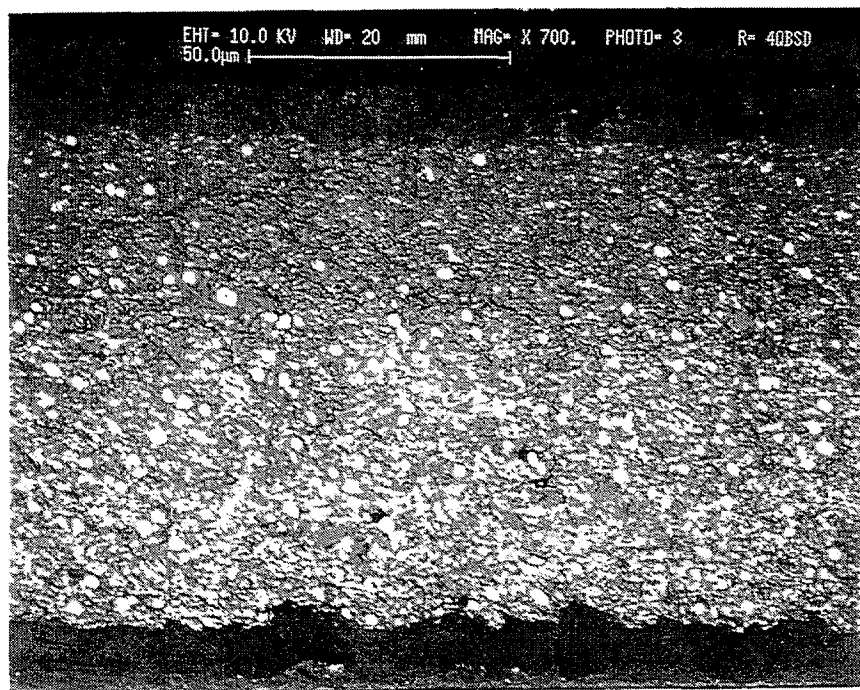EHT= 10.0 KV   WD= 21 mm   MAG= X 4.00 K PHOTO= 1   R= 40BSD
10.0μm

b

Figure 5. SEM images of a cross section of film containing mass fraction of 54 % lead: a) x700, and b) x4K.
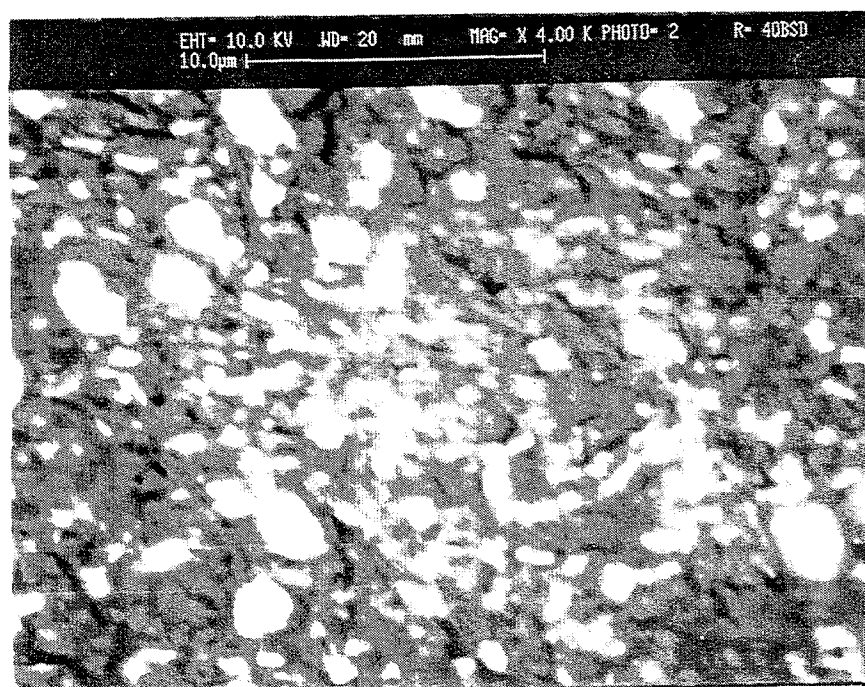
Figure 6. SEM images of a cross section of film containing mass fraction of 71 % lead: a) x700, and b) x4K.
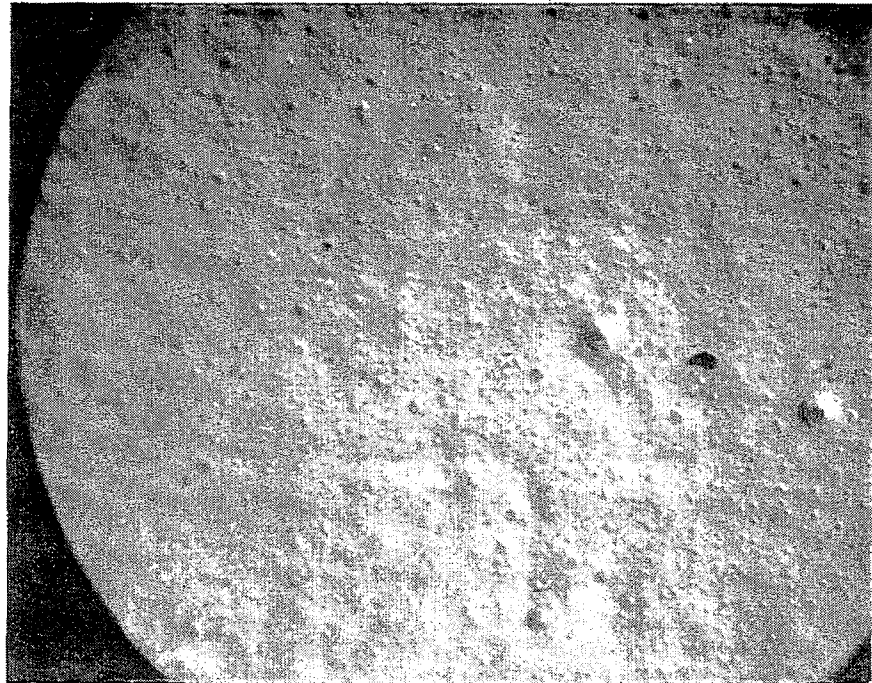
Figure 7. Light microscopic images of encapsulant surfaces: a) epoxy, and b) acrylic.

3.3 Lead Leaching Results

3.3.1 Unencapsulated Lead-Based Film

3.3.1.1 Effect of Type of Lead Pigment in Lead-Based Film

Figures 8 and 9 display the results of lead leaching at pH 4 and 10 from unencapsulated lead-based film containing a lead chromate or a basic lead carbonate pigment. Due to the extremely low level of lead leaching from these specimens; a graphite furnace AA spectrometer (instead of a flame AA spectrometer) was used to measure the lead contents in these leaching solutions. In these experiments, a commercial alkyd paint was used to dilute the lead paste. The amount of lead was approximately 20 % of the dry mass of the films. The amounts of lead in the films were calculated based on the amount of lead in the pigment, the pigment concentration, and the film density, as described in the Experimental Section.

Figure 8. Lead leaching results at pH 4 and 10 for an alkyd paint film containing a lead chromate pigment.

16

Figure 8 shows that little lead has leached from lead chromate-based films at pH 4 or 10. For the lead carbonate-based film, a small amount of lead was removed from the film in pH 10 solution and a sizable amount has leached out after 150 hours of immersion at pH 4 (Figure 9). Based on these results, lead carbonate pigment was chosen for subsequent leaching tests.
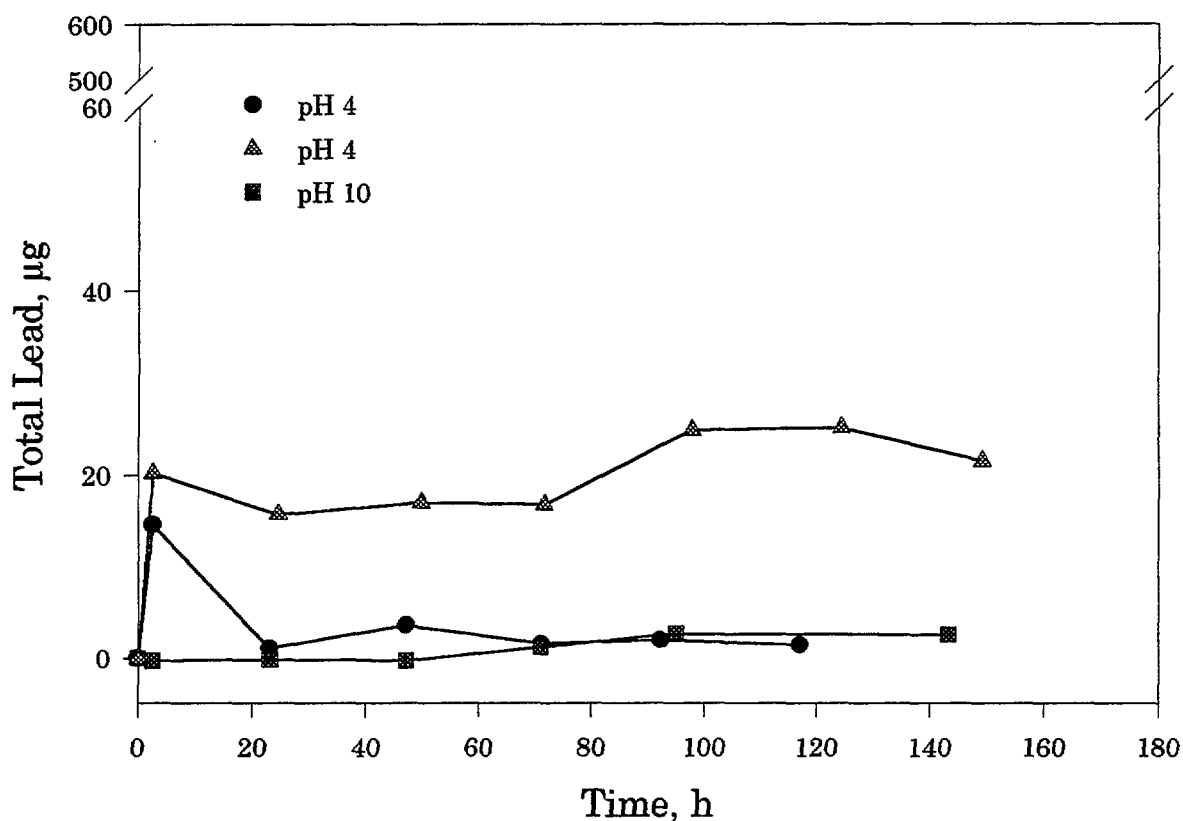
3.3.1.2 Effect of Solution pH on Solubility of Lead Carbonate Pigment

Although the solubility of lead carbonate in neutral water is known (6), solubility data at other pH values are lacking. The solubility of lead in a solution is defined as the mass of lead dissolved in the solution at saturation; it is expressed in concentration, i.e., grams of lead (Pb) per liter of solution. The effect of pH on the solubility of a resin-free lead carbonate pigment was investigated. In this study, the solubility of resin-free basic lead carbonate pigment was measured by the FAA technique. This experiment employed the same basic lead carbonate pigment used for lead-based films and the setup shown in Figure 2. HNO_3 and $NaOH$ provided pH 4 and 10 solutions, respectively. Solubility samples were prepared by placing 3.02 g of basic lead carbonate pigment in a glass container containing 500 ml of distilled water. After thoroughly stirring for one hour, 5 mL of the solution were taken from the solution at different times, filtered through a 0.2 μm pore size filter, and the supernatant was analyzed.
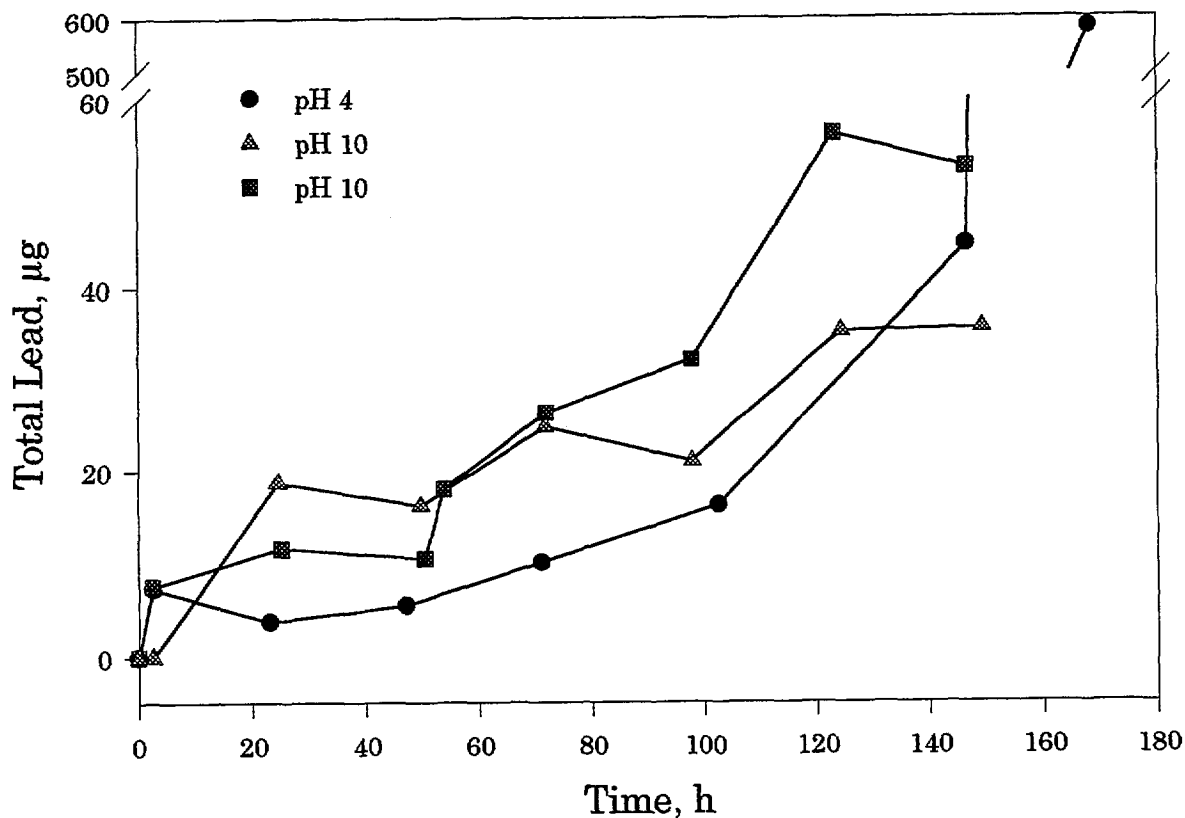
Figure 9. Lead leaching results at pH 4 and 10 for an alkyd paint film containing a lead carbonate pigment.

17
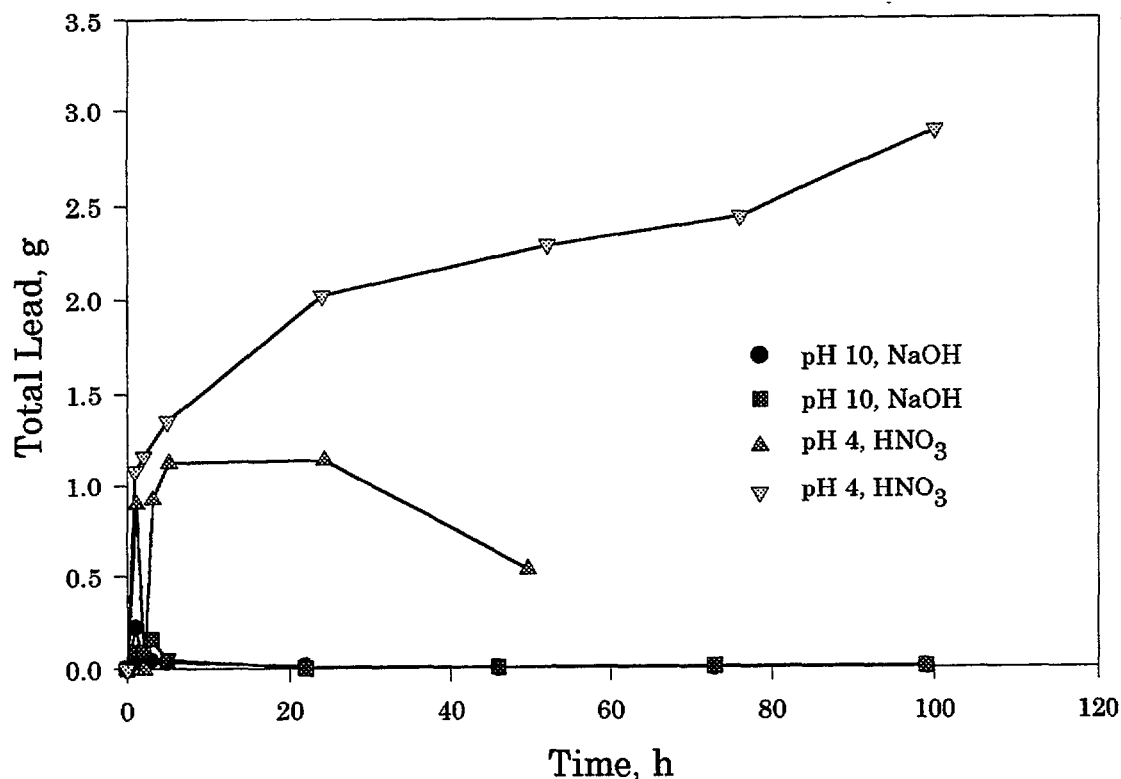
Figure 10. Solubility of lead carbonate pigment at pH 4 and 10.

Figure 10 presents solubility results of the lead carbonate pigment at pH 4 and 10. As can be seen, more lead was dissolved at pH 4 than at pH 10. After 100 hours in solution, about 3 grams of lead from the basic lead carbonate was dissolved in HNO_3 solution at pH 4, but essentially no lead was detected in the NaOH solution at pH 10. Further, at pH 4 basic lead carbonate pigment dissolved rapidly in the first 5 hours, and the dissolution appeared to level off after 20 hours.

3.3.1.3 Effect of Solution pH and Lead Concentration in the Films

The effects of pH at 2,4 and 10 on the leaching of lead from a linseed-oil film containing a mass fraction of 54% lead is shown in Figure 11. This film used lead carbonate as the pigment and HNO_3 and NaOH provided the selected pH solutions. The results show that a larger quantity of lead leached out at pH 2 than any other pH and that the amount of lead leached out increased with increasing immersion time. These results are consistent with solubility data of the resin-free pigment (Figure 10). However, even under the most favorable leaching conditions, i.e., pH 2 and long immersion time, the amount of lead leached from the 54% mass fraction lead-based film was still less than 5% of the initial content of lead in the film.

pH 2
pH 4
pH 4
pH 10

% Lead Leached from Coating

Time, h

Figure 11. Effect of pH on lead leaching from film containing mass fraction 54 % lead.

The diffusion of a substance through a membrane is inversely proportional to the square of the membrane thickness. That is, if a membrane thickness is reduced by one half, its diffusion rate will incre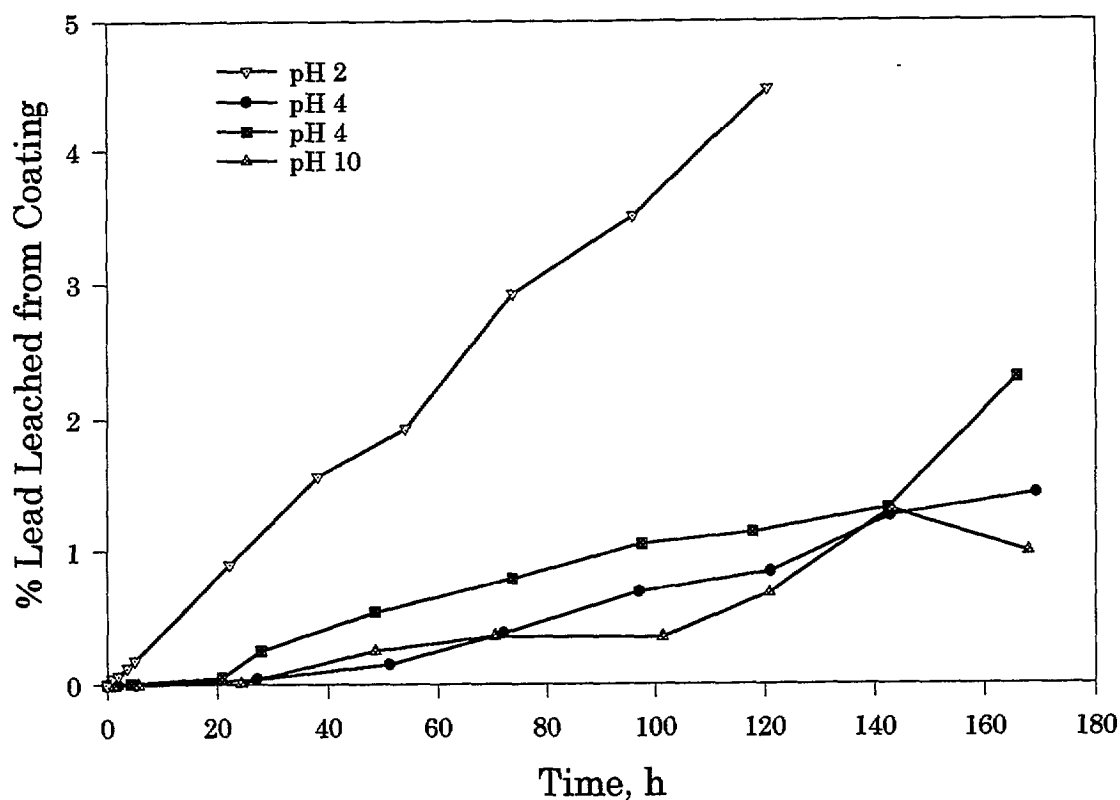ase by a factor of four. Thus, the rate of lead diffusion from the film to the solution is expected to increase if the thickness of the resin layer around each lead pigment particle is decreased. One way of reducing the thickness of this layer is to increase the pigment concentration in the film. For that reason, we investigated the effect of pH on the leaching of lead from a paint film containing a higher lead concentration.

Figure 12 presents the leaching of lead from a linseed-oil film containing a mass fraction of 71 % lead at pH 2 and 12. The results show a very small amount of lead leached out of the films at these pH values. For example, less than 1.5 and 3 % lead has leached out at pH 12 and pH 2, respectively, after 160 hours immersion. Figures 11 and 12 indicate that, in contrast to the resin-free lead pigment, pH did not appear to play an important role in the leaching of lead from films containing high or low lead concentrations. It should be emphasized that the pH range selected for this study is within the range of chemicals typically used in the households. For examples, the pH of a cooking vinegar is 2.5 while the pH of ammonia-based materials used for cleaning is 12.5. The result of the effect of pH on leaching provides an indication whether lead may leach from a lead-based paint if a household chemical accidentally comes into contact with the paint.
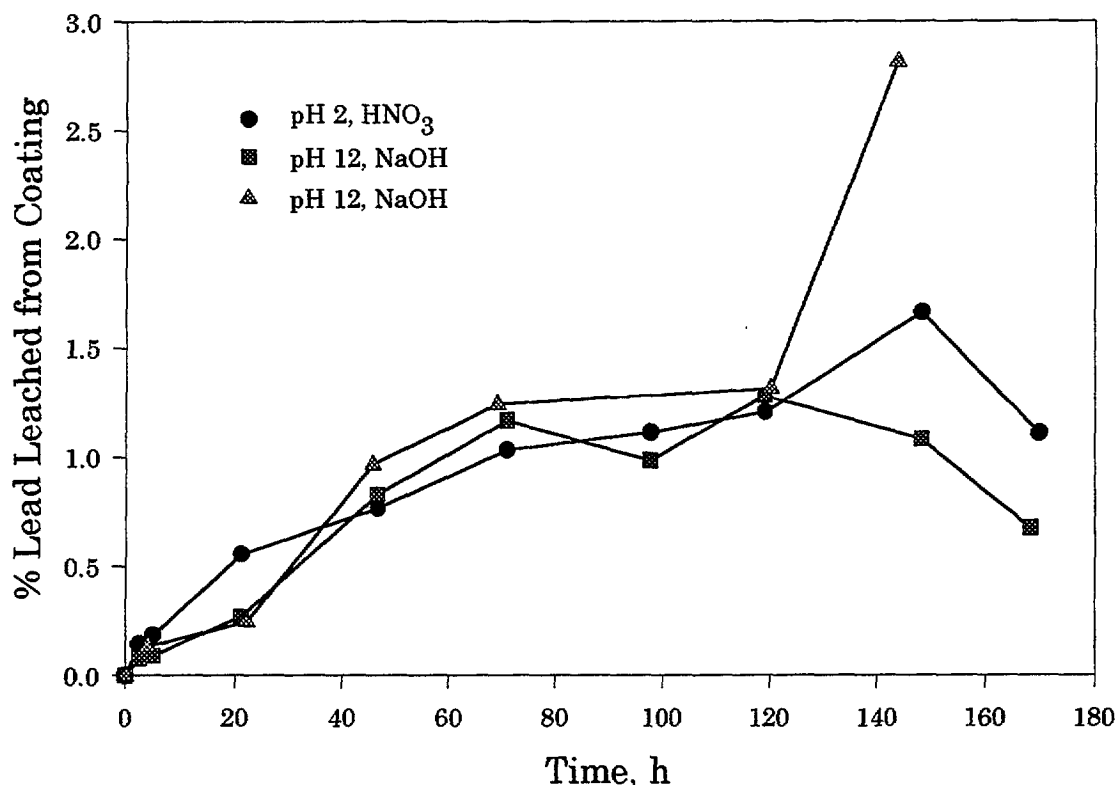
Figure 12. Effects of pH on lead leaching from film containing mass fraction 71 % lead.

3.3.1.4 Effect of Solution Chemical

Nitric acid is known as a good solvent for lead carbonate (5). However, the results of Figures 11 and 12 indicated that only a very small amount of lead was removed from a lead-based paint in HNO_3 solution after prolonged immersion even at pH 2. Because we want to investigate the transport of lead through encapsulant films, we searched for other agents that could leach lead more quickly from the lead-based films. Figure 13 compares lead leaching results from a linseed-oil film containing a lead-carbonate pigment immersed in different chemical solutions at pH 2 and 12. Data for HNO_3 at pH 4 and NaOH at pH 10 are also included for comparison. The amount of lead in these films was approximately 71% based on the mass of the dry film. As before, the amounts of lead leached are expressed with respect to the initial mass of lead in the films. As can be seen from Figure 13, only a very small amount of lead has leached out in ammonia or NaOH solution. These results imply that there is little chance of lead leaching from a lead-based painted wall after the wall is soaked for a long time in an ammonia cleaning solution.

Figure 13, however, shows that nearly 70% of the lead has leached out of the film within a few hours in the acetic acid solution at pH 2 (3.5 moles acetic acid in 1 liter of water). Further, the

amount of lead leached in the acetic acid solution was many times higher than that in the nitric acid. Evidence of both quantity and rate results indicate that acetic acid was a much more efficient leaching agent than nitric acid. It is noted that not only acetic acid but also lead acetate, a product of the reaction of lead and acetic acid, is capable of dissolving lead (5). Based on these results, a leaching solution containing 3.5 moles of acetic acid in 1 liter of water was chosen for studying the leaching of lead from lead-based films covered with an encapsulant.

It is interesting to note from Figure 13 that the amount of lead leached to the acetic acid solution appeared to remain constant after a short initial immersion time. This was confirmed in a repeated experiment. One reason for this may be that most of the lead in the film has been removed within a short exposure time. Further exposure apparently removed only a small additional amount of lead and that may be attributed to sampling error. Other possible reasons include a saturated lead acetate layer formed at the leaded particle/resin matrix interface thus preventing further lead dissolution, or a blockage of the transport routes in the resin matrix by the precipitated lead acetate.
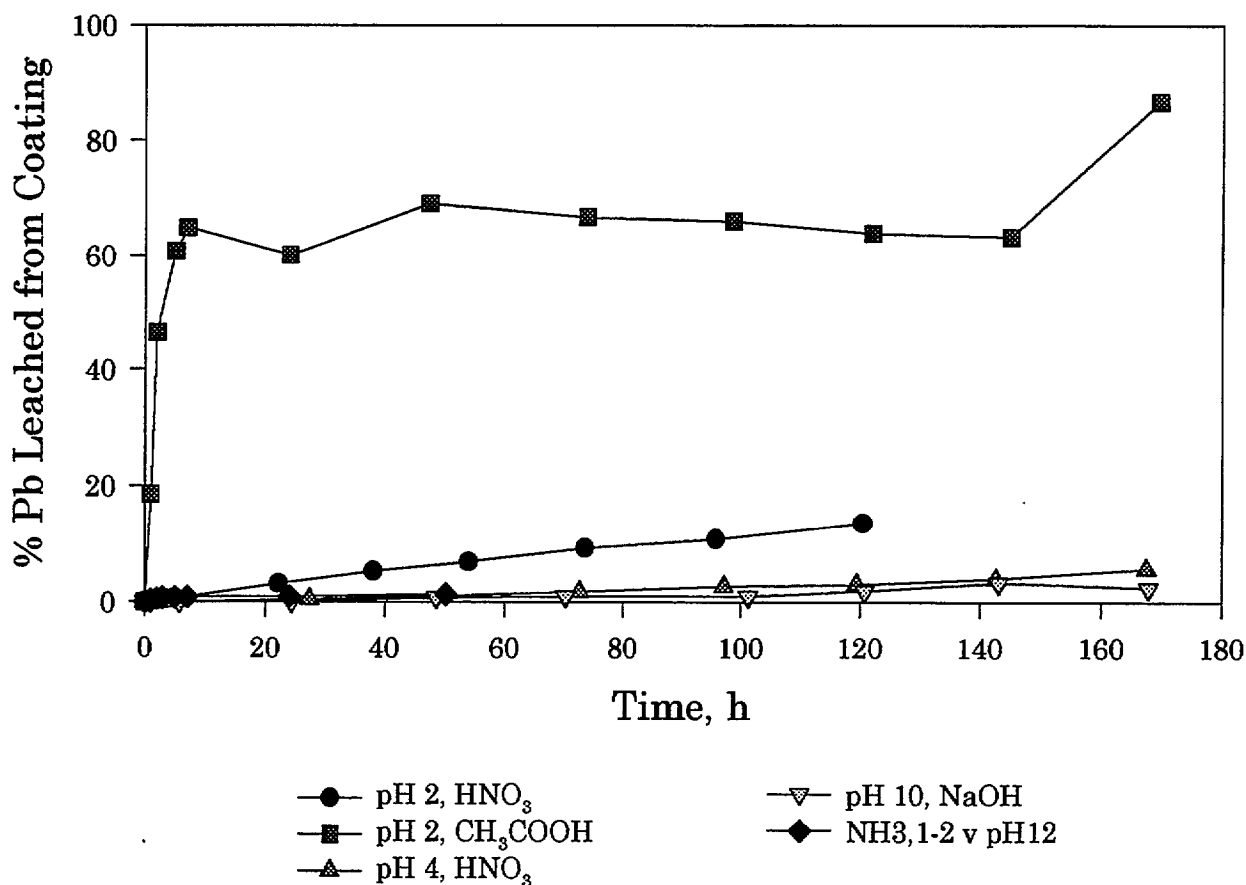

Figure 13. *Effects of solution chemical on lead leaching from lead-based film.*

3.3.1.5 Lead Leaching from Lead-Based Film Immersed in Vinegar

Figure 13 results suggest that lead from a lead-based paint may migrate to its outside surface if the lead-based paint comes into contact with a vinegar (vinegar contains about 0.8 moles of acetic acid in 1 liter of water). To verify this, we placed a 54% mass fraction lead-based film specimen in a horizontal ATR trough containing 3 ml of a vinegar solution and analyzed the vinegar solution *in situ* as a function of time by FTIR-MIR. The rationale for this experiment was that if lead acetate is detected in the solution, then acetic acid from the vinegar must have diffused into the film and reacted with the lead particle to form lead acetate, which migrates from the film to the solution. By examining the depletion of the C=O band of the acetic acid (about 5% in vinegar) and the growth of the carboxylate group (-COO⁻) of lead acetate in the solution, the conversion of acetic acid to lead acetate could be studied. This is exactly what was observed in the difference spectra presented in Figure 14 for two immersion times. These spectra were acquired by subtracting the FTIR-MIR spectra of vinegar solution in the ATR trough before immersing the lead-based film from those collected after different immersion times. Bands above or below the baseline of a difference spectrum indicate an increase or a decrease, respectively, of the concentration of a chemical functional group. The intensity of the band at 1716 cm⁻¹, due to C=O of the acetic acid, decreased while the intensity of the band near 1548 cm⁻¹, due to COO⁻ of the lead acetate, increased. Other bands also changed as a result of the acetic acid /lead acetate conversion as well. For example, the intensity of the band at 1278 cm⁻¹ decreased and those at 1424 cm⁻¹, 1024 cm⁻¹ and 972 cm⁻¹ increased. Assignments of these bands were beyond the scope of this study.
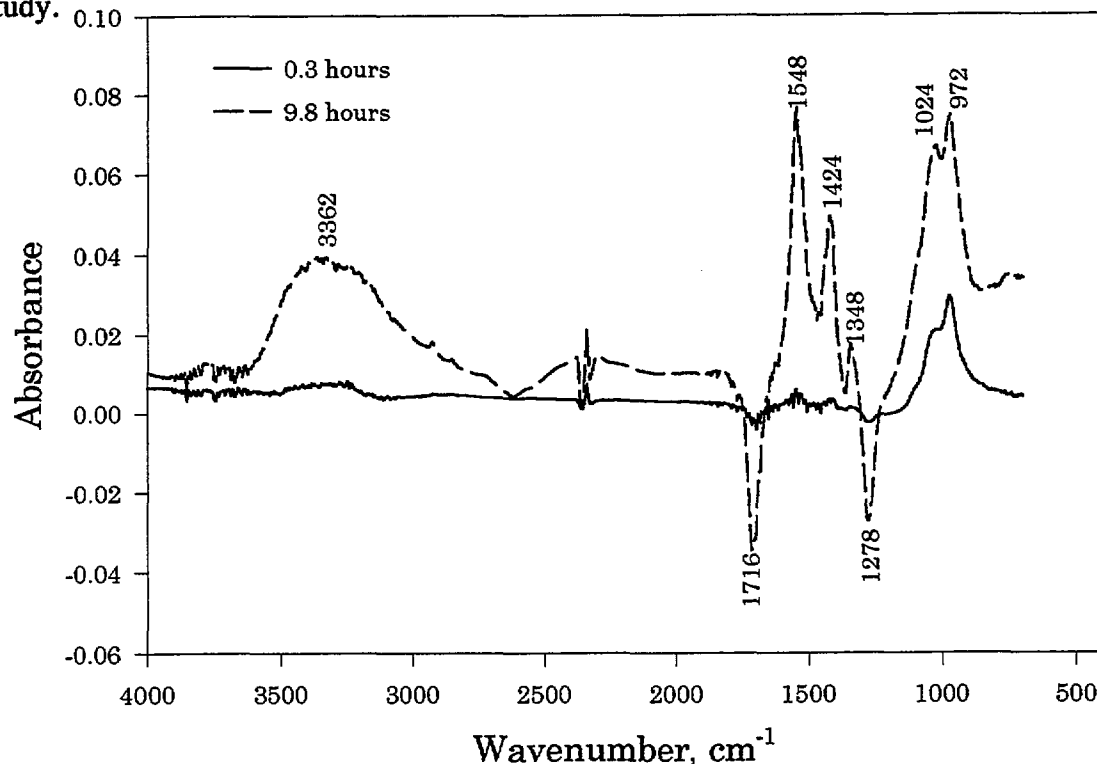

Figure 14. Effect of immersion of a lead-based film on FTIR spectra of a vinegar solution.
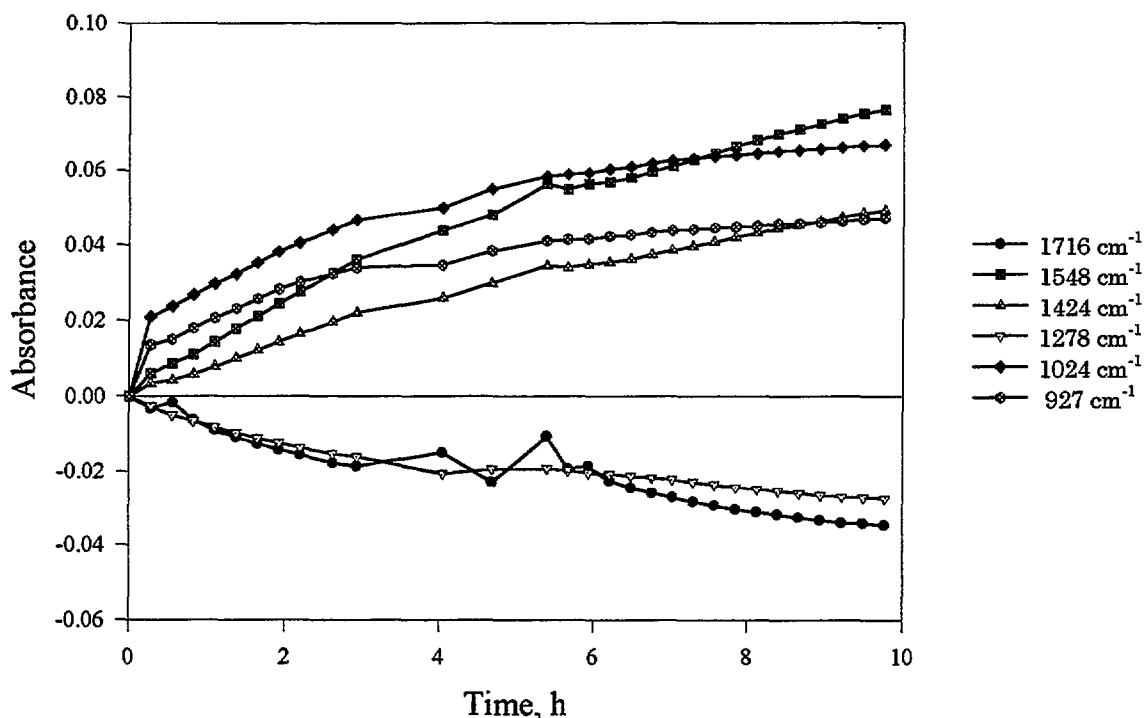
Figure 15. Intensity changes of several FTIR bands of a vinegar solution after immersing a lead-based film in it.

Figure 15 displays change in the intensity of various FTIR bands as a function of exposure time of the 54 % mass fraction lead-based film immersed in a vinegar solution. As can be seen, the conversion of acetic acid (C=O band at 1716 cm^{-1}) to lead acetate (COO$^-$ band at 1548 cm^{-1}) was rapid at first, then slowed down. Since the intensity of an infrared band is proportional to the amount of a functional group, these results could be used to estimate the diffusion coefficient of acetic acid from a vinegar solution migrating into, and of lead acetate leaching from, a lead-based film using the sorption approach. The determination of the diffusion coefficients of acetic acid and lead acetate in lead-based and encapsulant films is presented in Sections 3.3.3 and 3.3.4.

3.3.2 Encapsulated or Painted Lead-Based Film

The results shown in Figure 13 for an unencapsulated lead-based film indicated that, for a lead-carbonate pigment and for the solutions investigated in this study, the leaching was greatest in an acetic acid solution at pH 2 (3.5 mol/L concentration). These parameters were used for studying the transport of lead through an encapsulated lead-based film (lead-based film with an encapsulant or a paint applied to it). In this experiment, encapsulated lead-based specimens were immersed in a 3.5 mol/L acetic acid in water solution and the concentration of lead in the solution was measured as a function of immersion time. Initially, Type I specimens (10 cm x10 cm

23

encapsulant/lead-based film/PMMA substrate) were used for this study. However, during the course of immersion the films were found to separate from the substrate even though the edges of these specimens were sealed with wax. The delamination occurred at the interface between the lead-based film and the PMMA substrate. This separation resulted in a direct contact between the unencapsulated side of the lead-based film with the leaching solution. This was unsatisfactory because, in that case, leaching of lead could also take place on the "unencapsulated" side of the films. For that reason, the setup shown in Figure 1b was used for the leaching of lead through an encapsulated lead-based film. This specimen configuration was found satisfactory because no evidence of delamination was observed on these specimens, presumably due to the attachment of the cylinder to the coated substrate. As indicated in the Experimental Section, the encapsulants were applied on the lead-based coated PMMA substrate using a 625 μm gap blade. The thicknesses of the dry epoxy encapsulant, acrylic encapsulant, and alkyd paint on the lead-based films were 230 μm, 350 μm, and 220 μm, respectively.

Figure 16 presents duplicate results on the leaching of lead through epoxy and acrylic-based encapsulants and alkyd paint using a pH 2, 3.5 mol/L acetic acid solution. These films contained a mass fraction of 54% lead and basic lead carbonate was used as the pigment. The amount of lead leached (vertical axis) was based on the initial mass of lead in the films, similar to that expressed for unencapsulated lead-based films. The experiment for the epoxy-based specimens was terminated after about seven hours of immersion because severe degradation (presumably hydrolysis) had occurred on these specimens. The degradation increased with immersion time, as evidenced by an increase in the cloudiness of the solution. After seven-hour exposure, the films lost integrity and were broken at several locations. However, delamination was not observed until after 24 hours of exposure. Thus, the effect due to a direct contact between the acetic acid and the unencapsulated side of the lead-based film was, at best, minimal within the measuring period (seven hours). The acrylic encapsulant and the alkyd paint also underwent degradation but at a much lower rate. For the alkyd paint specimens, the areas around the stirring bars were delaminated after 50 hours of immersion; no measurement was recorded after this time.

Figure 16 demonstrated that a majority of lead from the lead-based films underneath the two encapsulants has leached out, similar to that for unencapsulated specimens. The experiment for the alkyd paint samples was terminated after 50 hours of immersion, as stated above. At this time, approximately 50 % of lead in the lead-based film of these samples has leached out. The rate for lead transport through the epoxy encapsulant was greatest while that for the alkyd paint was lowest; the acrylic was in between. For the acrylic specimen, the amount of lead buildup in the leaching solution appeared to remain constant after 50 hours of exposure. A comparison between Figures 13 and 16 shows that, while lead leached from the unencapsulated films almost immediately after immersion in a 3.5 mol/L acetic acid, there was an induction period needed before lead was removed from the encapsulated samples.
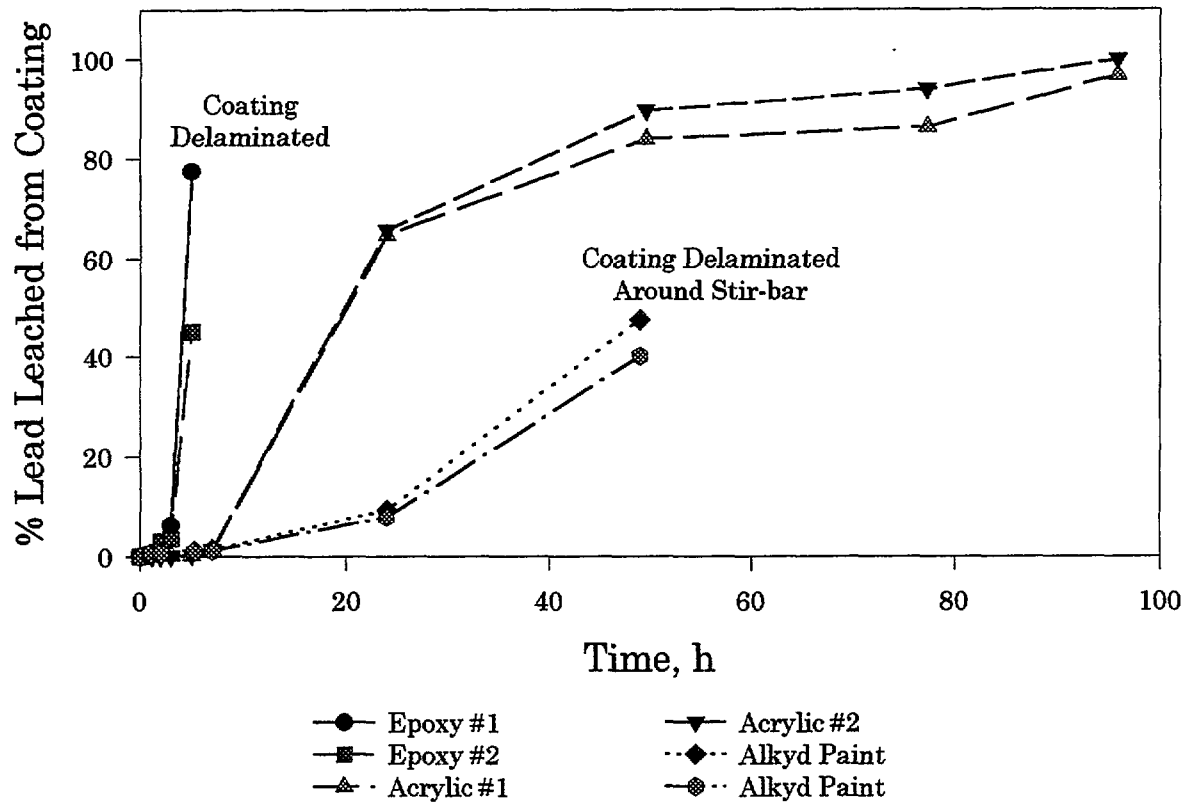
Figure 16. Lead leaching results of a lead-based film under encapsulants and alkyd paint immersed in 3.5 mol/L acetic acid.

To provide an explanation for the effectiveness of acetic acid for leaching lead from an unencapsulated or encapsulated lead-based film, we must understand how lead can be transported through the films. The following discussion is for an unencapsulated lead-based film. The same rationale can be applied for encapsulated films, since the organic constituents of encapsulants are similar to those of lead-based paint films. As indicated earlier, each leaded particle in a lead-based film is covered with a layer of the resin. For lead to leach out from a lead-based paint film, several processes must take place. First, the attacking chemical species must migrate inward from the solution through the resin matrix to reach the lead pigment particles; second, the leaded particle must be dissolved by the leaching solution (to form a lead compound on the surface of the lead particles); and third, the formed lead compound(s) must be transported outward through the resin matrix to the solution. The second process is a function of the reactivity between the leaching agent and leaded particle. The first and last processes depend strongly on the diffussivities of the leaching agents and lead compounds through the resin matrix.

The second process should not be the determining factor in the leaching of lead from the lead-based films to the solution because the reactivity of acetic acid toward lead carbonate is high. Indeed, the free energy of formation of lead acetate is highly negative (-225 J/mol) (7), indicating

25

that formation of lead acetate is favored. For a comparison, the free energy of formation for lead nitrate is four times less than that of the lead acetate, suggesting that the reactivity of lead toward nitric acid is substantially less than that of lead toward acetic acid.

The main factor responsible for the effectiveness of the acetic acid as a leaching agent for lead probably lies with the first and third processes, i.e., the diffusivities of acetic acid and its lead derivative in the resin matrix. To verify this postulation, we conducted several experiments to measure the diffusion coefficients of acetic acid and lead acetate in lead-based films and acetic acid in encapsulants using the uptake approach. In this approach, the weight gain as a function of time can be used to determine the diffusion coefficients of the solutions in a polymer film, using Fickian equations.

3.3.3 Measurement of Diffusion of Acetic Acid in Lead-Based and Encapsulant Films

For 100 % acetic acid, the weight gain as a function of time could not be recorded for some encapsulants because the uptake of acetic acid was so fast that it was not possible to handle the specimens. Instead, we recorded the swelling of the specimens and used these data to estimate diffusivity of 100 % acetic acid in lead-based films and encapsulants. This is possible because the swelling of a solid in a solution only occurs if the solvent has sufficient affinity for the polymer films to spontaneously form "solid solutions", which are accompanied by an evolution of heat (8). If the solvent is held only on pre-existing surfaces of rigid pores of a solid, no heat is generated and no or little swelling occurs. Thus, swelling is directly proportional to the amount of uptake of the solvent in a solid. The swelling experiment was conducted by immersing each lead-based or encapsulant free film specimen in a container containing 100 % acetic acid solution. Specimen dimensional changes were followed and analyzed via a video-computer image analysis system, as described in the Experimental Section.

Figure 17 depicts the swelling behavior of the fully-cured epoxy and acrylic encapsulants, the alkyd paint, and the 54 % mass fraction lead-based films in 100 % acetic acid. The thickness of the lead-based free film was 54 μm $\pm$ 7 μm, and those of the alkyd paint, epoxy encapsulant, and acrylic encapsulant were 70 μm $\pm$ 2 μm, 80 μm $\pm$ 7 μm, and 74 μm $\pm$ 5 μm, respectively. Both epoxy and acrylic encapsulants swelled substantially within a short exposure time. These specimens almost doubled their sizes within a few minutes. The alkyd encapsulant swelled much less, approximately 25 % after 10 minutes. The lead-based linseed-oil film swelled about 60% of its original size after 10 minutes. It is interesting to note that only the acrylic encapsulant continued to slowly swell after the initial short period. After three hours, this encapsulant had almost tripled its size. The diffusion coefficients of 100 % acetic acid in the lead-based and alkyd paints and encapsulants were determined using these swelling data.

The diffusion coefficient, expressed in cm^2/sec, is defined as the rate of transfer of the diffusing substance across a unit area of a section, divided by the gradient of concentration of the section.
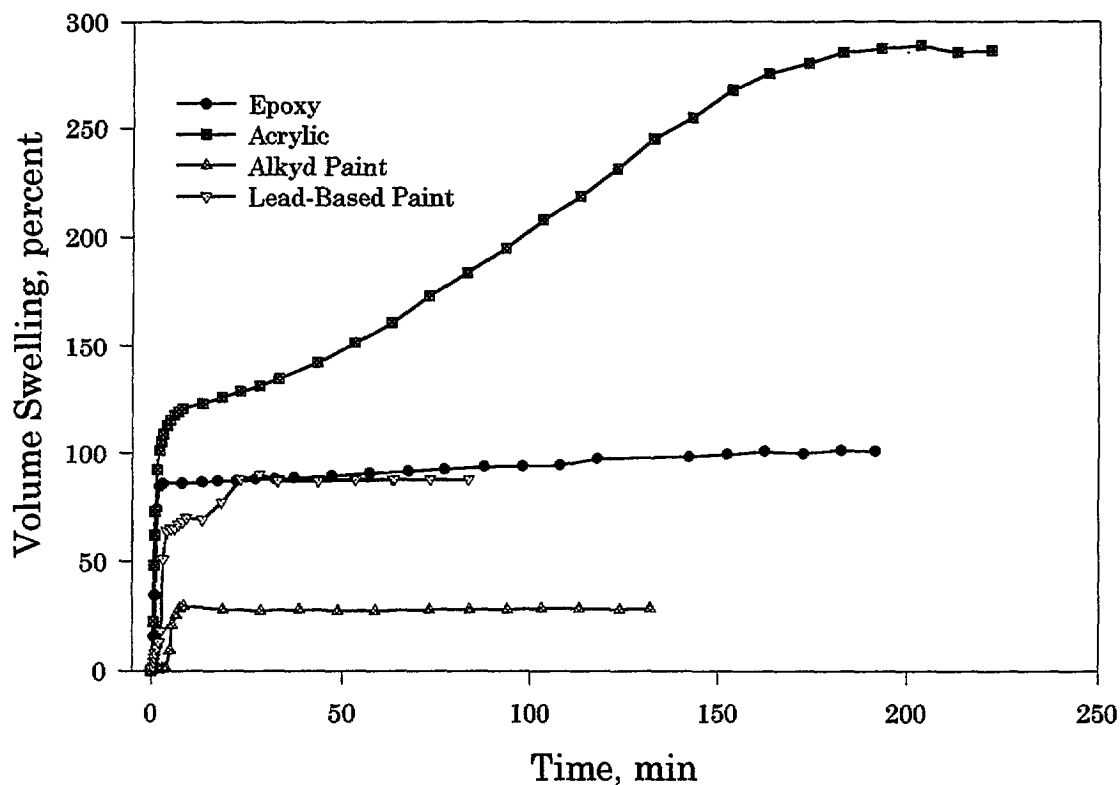
Figure 17. Swelling behavior of encapsulants, alkyd paint, and lead-based film immersed in 100 % acetic acid.

If the diffusant concentration within the film surface is initially constant, then the amount of the diffusant, M_t, taken up after time t, by a film of thickness l is governed by (9):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[\frac{-(2n+1)^2\pi^2 D_{eff}\, t}{4l^2}]$$

$$(1)$$

where M_∞ is the equilibrium mass after infinite time, D_{ff} is the effective diffusion coefficient expressed in cm^2/sec, and n is an integer. Equation 1, with proper interpretation of M_t and M_∞, can also be used for obtaining the diffusion coefficient from desorption data. The value of D_{eff} can be deduced from the initial stage of a graph of M_t/M_∞ as a function of t/l^2. As indicated earlier, the amounts of acetic acid taken up by the films as a function of time could not be obtained. However, percent swelling, which is directly related to amount uptake, was measured and these results were used to calculate the effective diffusion coefficient, D_{eff}. Using swelling notations, Equation 1 may be written

27

$$\frac{S_t}{S_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 D_{eff}\, t}{4 l^2}\right] \quad (2)$$

where S_t is the fraction swelling at time t and S is the fraction swelling after infinitive time (maximum swelling).

Figure 18 presents plots of S_t/S_∞ versus t/l^2 for encapsulants and lead-based paints. Values of l taken before immersion were used for all films. Values of D_{eff} can be conveniently deduced at the half-equilibrium time, by using the following expression (9):

$$D_{eff} = \frac{0.0492}{(t/l^2)_{1/2}} \quad (3)$$

where $(t/l^2)_{1/2}$ is value of t/l^2 at S_t/S_∞ = ½ (from Figure 18). The error due to this approximation has been found to less than 0.001 percent (9). Except for the epoxy encapsulant where a t/l^2 value at S_t/S_∞ = 1/4 was used, the diffusion coefficients of 100 % acetic acid in the encapsulants and lead-based films were obtained by substituting t/l^2 values at S_t/S_∞ = ½ from Figure 18 into Equation 3. The results are given in Table 2.
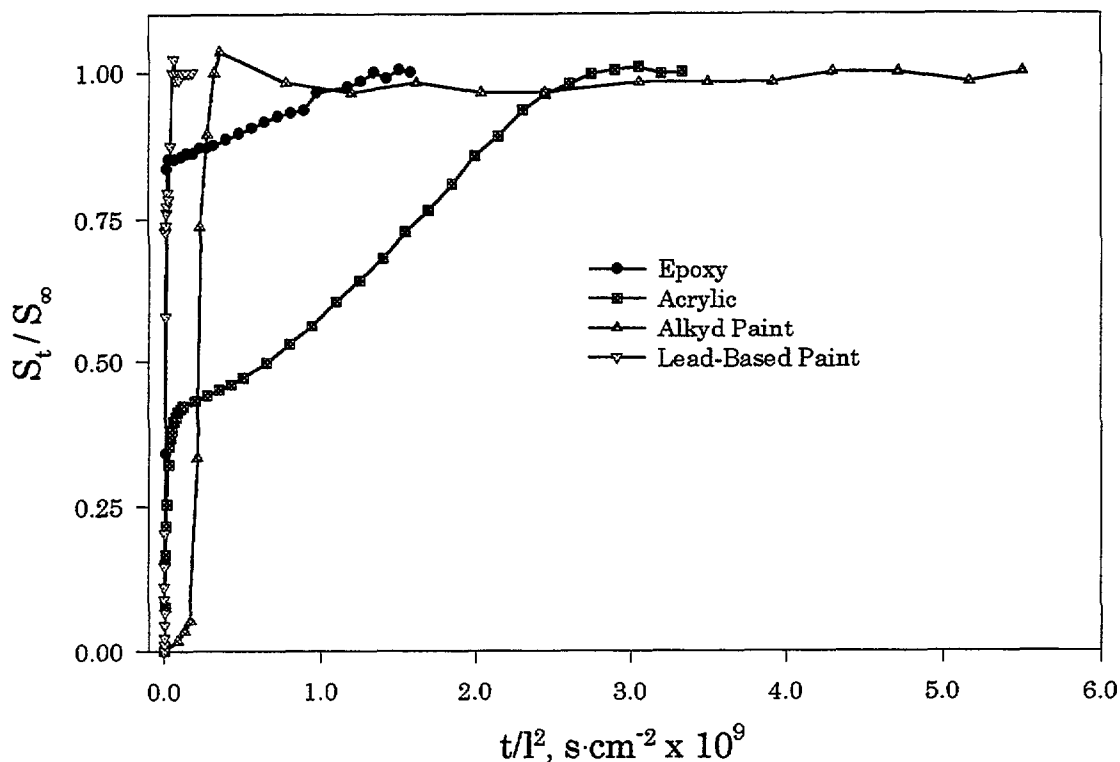

Figure 18. Plots of S_t/S_∞ versus t/l^2 for encapsulants, alkyd paint, and lead-based film immersed in 100 % acetic acid.

Table 2. *Diffusion coefficients of acetic acid in encapsulants and a lead-based film, of lead acetate in a lead-based film, and of other solvents in polymers*

Film	Diffusing Species	Diffusion Coefficient, cm^2/s	Reference
Epoxy encapsulant	100% acetic acid	4.7×10^{-9} (22 °C)	this work
Acrylic encapsulant	100% acetic acid	2.8×10^{-11} (22 °C)	this work
Alkyd paint	100% acetic acid	2.3×10^{-10} (22 °C)	this work
Lead-based linseed oil	100% acetic acid	8.8×10^{-9} (22 °C)	this work
Lead-based linseed oil	acetic acid from a vinegar solution	1.2×10^{-10} (22 °C)	this work
Lead-based linseed oil	lead acetate formed from a vinegar solution	1.44×10^{-10} (22 °C)	this work
Poly(vinyl acetate)	acetone	1.3×10^{-11} (40 °C)	(11)
Poly(vinyl acetate)	methyl alcohol	1.5×10^{-9} (25 °C)	(11)
Poly(methyl acrylate)	methyl acetate	1.0×10^{-9} (25 °C)	(11)
Poly(methyl acrylate)	ethyl acetate	6.0×10^{-10} (25 °C)	(11)
Organic coatings	water	$1-5 \times 10^{-8}$ (22 °C)	(10)

The diffusion coefficients of 100 % acetic acid in the lead-based paint and the epoxy encapsulant are relatively high, 10^{-9} cm^2/s. They are almost two orders of magnitude higher than that in the acrylic encapsulant. The value for acetic acid in the alkyd paint was in the 10^{-10} cm^2/s range. For a comparison, the diffusion coefficients of water in organic coatings are on the order of 10^{-8} cm^2/s (10). Unfortunately, no values of D for 100 % acetic acid in organic coatings or polymer films were found in the literature. However, there are some D data for other relevant solvents, such as, methanol and acetone (11); these values are included in Table 2 for comparison. The results show that D values for acetic acid in the encapsulants, the alkyd paint, and the lead-based films obtained in this study are reasonable and within the range reported for other similar organic solvents in polymers.

There were, at least, two factors that may have affected the diffusion coefficients of 100 % acetic acid in the encapsulants and the lead-based films. The first one was the hydrolytic degradation of the films, as indicated earlier. The degradation would reduce the thickness of the layer through

which the acetic acid molecules must transport to reach the leaded particle. This would certainly accelerate the diffusion process. The second factor was the swelling of the film. In using Equation 1, the thickness of the film was assumed to be constant as the diffusion proceeded. However, the films swelled and the thickness increased as acetic acid entered. In this case, Equation 1 is still valid provided that a constant frame of reference, e.g., total mass of the system, is used (12). In general, the diffusion in swollen films is greater than that in unswollen films (13).

3.3.4 Measurement of Outward Diffusion of Lead Acetate Formed by a Vinegar in a Lead-Based Film

The diffusion coefficient of lead acetate from a lead-based paint was determined. The data used for this measurement came from an FTIR *in situ* experiment for a mass fraction of 54 % lead-based film immersed in a vinegar solution, as described in the Experimental Section. The results are displayed in Figures 14 and 15. The intensity change of the band at 1548 cm^{-1} of lead acetate in solution was used for the diffusion coefficient determination. Since FTIR intensity is directly proportional to the concentration of a material, it can be used to represent the amount of material taken up or desorbed (e.g., M_t in Equation 1). Using the FTIR intensity notation, Equation 1 may be written for lead acetate diffusing from a lead based film:

$$\frac{I_t}{I_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 D_{eff}\ t}{4l^2}\right] \quad \textbf{(4)}$$

where I_t is the intensity (measured as peak height) of the 1548 cm^{-1} band of the lead acetate at time t and I_∞ is that of the same band at infinite time. Equation 4 is valid only if the amount of lead acetate desorbed from the film is approximately equal to the amount of lead acetate buildup in the solution. This assumption is reasonable since lead acetate is highly soluble in water at room temperature (5). Note that both I_t and I_∞ are the intensities of the lead acetate buildup in the leaching solution. Figure 19 presents plots of I_t/I_∞ versus t/l^2 for the 1548 cm^{-1} band. The diffusion coefficient D was determined by substituting t/l^2 values at $I_t/I_\infty = \frac{1}{2}$ of Figure 19 into Equation 4.

Following this procedure, the effective diffusion coefficient of lead acetate leaching from a 54% mass fraction lead-based film was found to be 1.4×10^{-10} cm^2/s (Table 2). This value agrees reasonably well with those of other acetates in poly(methyl acrylate) films reported in the literature (14) (Table 2). Using the same procedure and the acetic acid band at 1716 cm^{-1}, the diffusion coefficient of acetic acid from a vinegar solution was calculated to be 1.2×10^{-10} cm^2/s. These results suggest that the diffusion of acetic acid from a vinegar solution into a lead-based film had approximately the same rate as that of lead acetate diffusion out of the film.
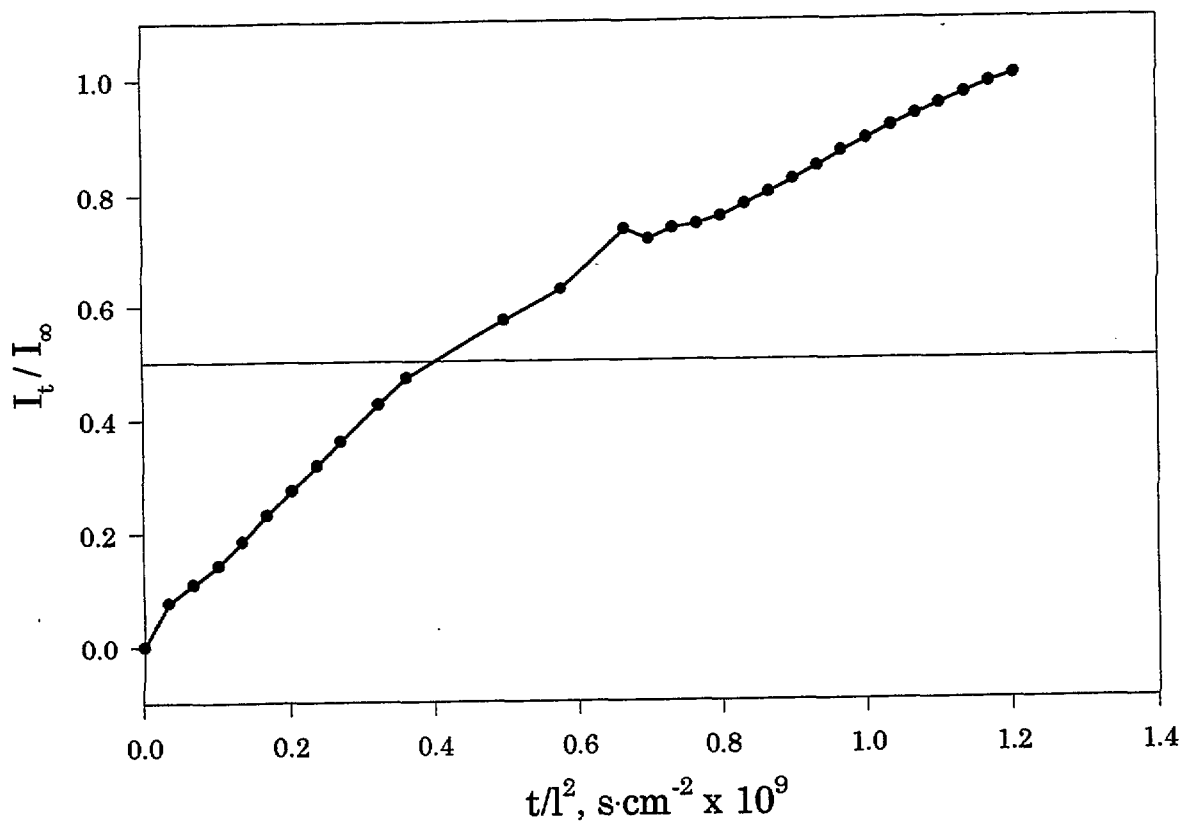
Figure 19. *Plots of I_t/I_∞ versus t/l^2 for a lead-based film immersed in a vinegar solution.*

It is evident from Table 2 that the diffusion coefficient in lead-based film of acetic acid from a 100 % concentration solution is about seven times greater than that from a vinegar solution (containing about 0.8 moles acetic acid in 1 liter of water). Before comparing these two values, several points should be emphasized. First, although the diffusion equations assume a concentration independence, concentration does affect the diffusion coefficients of solvents in polymer films (13). Second, in a 100% acetic acid solution the films underwent substantial hydrolytic degradation, as stated earlier. This would decrease the film thickness and increase the diffusion coefficients. Very little swelling and no evidence of hydrolytic degradation were observed for films immersed in the vinegar solution. And third, there may be other unknown components in the vinegar solution that may affect the diffusion rate of acetic acid. Further work is needed to investigate the effects of acetic acid concentrations on the diffusion of acetic acid into, and the corresponding lead acetate out, of the films before a conclusion can be drawn whether a lead acetate diffusion out or an acetic acid migration into the film is the controlling factor of the lead leaching from a lead-based film with and without an encapsulant.

31

The determination of the diffusion coefficients of leaching agents into, and of lead derivatives out of, a lead-based film with and without encapsulants is important in determining 1) the effectiveness of a lead leaching agent, 2) the ability of an encapsulant to prevent the leaching of lead from a lead-based film, and 3) the time it takes for lead to leach out when a lead-based film comes into contact with a leaching agent. For example, using the diffusion coefficients for acetic acid and lead acetate from a vinegar solution given in Table 2, it is estimated that it would take approximately 24 hours for lead under a resin layer of 100 μm (4 mils) immersed in a vinegar solution to leach out to the film surface. It would take four times longer for lead to leach out if an encapsulant having the same thickness and diffusivity was used to cover the lead-based film.

Both the leaching and diffusion measurement results obtained from this study indicate that acetic acid is a possible candidate to use as a leaching agent to characterize the transport of lead through encapsulants. Acetic acid at a concentration of 3.5 mol/L effectively leaches lead from the lead-based films, both with and without an encapsulant. However, it also quickly degraded the encapsulants used in this study. Because 3.5 mol/L acetic acid solution is a much stronger organic acid than would be expected to be present in household environments and a potential test should not cause a different mode of degradation than expected in service use of a product, further study is needed to investigate the effect of acid concentration on leaching rate of lead from lead-based paints and through encapsulants.

4 CONCLUSIONS

Lead in paints has been associated with lead poisoning in children. Coating lead-based paint with a polymeric encapsulant is a potential abatement method for controlling the hazards associated with lead-based paints. Before these benefits can be realized, however, issues concerning leaching of lead from the underlying lead-based paint layer through the encapsulant film to its surface must be addressed. The objective of this study was to provide a technical basis for the development of a standard test method for lead leaching through polymeric encpasulants. To that end, the effects of variables including lead pigment type, lead concentration, chemical types and pH of the leaching solutions, and types of encapsulants on the leaching of lead from a lead-based film with and without an encapsulant were investigated. Following are the conclusions of major findings of this study.

1)   An experimental setup consisting of a cylinder attached to lead-based film, with and without an encapsulant, applied to a poly(methyl methacrylate) (PMMA) substrate was suitable for studying the leaching of lead from lead-based paints.

2)   A pH controlled system was effective for controlling the pH of leaching solutions.

3)   Little (<5 %) lead leached from a linseed-oil film containing lead chromate or lead carbonate immersed in inorganic acids or bases in the pH range between 2 and 12. Based on this result, these acids were not considered suitable for measuring transport of lead

through encapsulants; the result also suggests that there is little chance that lead may leach from a lead-based painted wall when the wall comes into contact with ammonia-based cleaning solutions.

4) Acetic acid at 3.5 mol/L concentration (pH 2) leached nearly 70% lead from a lead carbonate-containing film within 5 hours. This is about 70 times greater than lead amount leached after 100 hours in a nitric solution of equal pH.

5) For lead-based films under an encapsulant, an induction period exists before lead was transported through the film in a 3.5 mol/L acetic acid leaching solution.

6) For the encapsulants and paint tested in 3.5 mol/L acetic acid solution, a substantial amount of lead leached from the lead-based film underneath encapsulants; the leaching rate was highest through the epoxy and lowest through the alkyd paint film.

7) Fourier transform infrared (FTIR) in the internal reflection mode provided a good method to follow the reaction of acetic acid and lead from the lead-based films. This spectroscopic data can be used for determining the diffusion coefficient of lead acetate from the film to the solution.

8) The diffusion coefficient of lead acetate formed from a vinegar solution in a lead-based film was found to be in the same range with other organic acetates, 10^{-10} cm^2/s.

9) Video-computer image analysis was found suitable for measuring the diffusion coefficients of 100 % acetic acid in lead-based paints and encapsulants; these values are in the 10^{-9} to 10^{-11} cm^2/s range.

10) Acetic acid at 3.5 mol/L concentration was found to be a possible candidate for investigating lead leaching from a lead-based film with and without an encapsulant, because it effectively leaches lead from lead-based films, unlike weak inorganic acids or bases. However, it also appears to cause a degradation of the encapsulants that may not occur during typical use of the products. Hence, further work is needed to investigate the leaching as a function of acetic acid concentration.

5 ACKNOWLEDGMENTS

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